



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 406 161 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **22.02.95** (51) Int. Cl.⁸: **C08F 299/02, C08F 283/06,
G02C 7/04, // (C08F283/06,
214:00)**
- (21) Application number: **90810428.4**
- (22) Date of filing: **12.06.90**

(54) Fluorine and/or silicone containing poly(alkylene-oxide)-block copolymers and contact lenses thereof.

(30) Priority: **20.06.89 US 368755
28.02.90 US 486493**

(43) Date of publication of application:
02.01.91 Bulletin 91/01

(45) Publication of the grant of the patent:
22.02.95 Bulletin 95/08

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(56) References cited:
**EP-A- 0 277 771
US-A- 4 528 301**

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Description

Two classes of contact lenses can be distinguished by the way they are fitted to the eye. In hard lenses the fit is flatter than the cornea itself and the lens rocks back and forth with each eye lid blink, pumping tear fluid and thereby oxygen, as well as cell debris under and from under the lens. Hard lenses are preferred whenever excellent visual acuity is desired and difficult vision corrections are required, for instance in the case of astigmatism. They are however less comfortable for the wearer than are soft lenses, the second class of contact lenses. Soft contact lenses derive their name from their low modulus and draping quality, which allows them to smoothly cover the cornea surface. They are fitted to match the cornea as closely as possible and they are not much disturbed by the eyelid. Because of their tight adherence to the cornea, they have to possess sufficient oxygen permeability to keep the cornea well supplied with oxygen.

In the most common soft lens material - ~ 40% water containing poly-(2-hydroxyethyl methacrylate) or poly-HEMA - water provides for sufficient oxygen flux to allow poly-HEMA lenses to be worn on a daily basis. The oxygen permeability O₂.DK of a poly-HEMA hydrogel with ~ 40% water is 6.5 barrers, and for hydrogels with higher water content, for example poly-(N-vinylpyrrolidone) or poly-(vinyl alcohol) copolymers it is ~ 12.5 at 50% water, 15.5 at 60% water and 25 at 70% water. Such higher water-content hydrogels allow therefore the manufacture of soft contact lenses for extended wear, up to several months, subject only to periodic cleaning. Unfortunately, high water content hydrogels are also very fragile, especially if they are cut very thin, as they often are in order to increase oxygen flux.

Another class of soft contact lens materials are polysiloxane rubbers (PDMSi), which can have O₂.DK values up to 500 barrers. Several polysiloxane based soft contact lens materials have been described, among them: conventional PDMSi rubbers produced by a hydrosilation cure; PDMSi-polyurethanes and PDMSi-polyacrylate block copolymers. All these materials suffer from an inherent lack of wettability and therefore require some kind of surface treatment to achieve the wettability required for comfortable and safe in-eye wear.

For non-hydrogel, water free contact lens compositions, siloxane units containing polymers have been used both, for soft contact lenses and hard contact lenses with enhanced oxygen permeability; fluorinated groups, which are another group of oxygenflux enhancing moieties, have only been used in hard contact lens materials although they would be preferable to siloxane groups in non-hydrogel soft lenses as well because of their low lipophilicity and low protein adsorption tendencies.

In hydrogel soft contact lens materials on the other hand, siloxane as well as fluorine has been used to enhance the oxygen permeability and many such silicone or fluorine containing hydrogels have been described in the literature for use as contact lens materials. Such silicone and/or fluorine containing hydrogels can possess oxygen permeabilities 3-8 times that of Si- or F-free hydrogels and at the same time retain some of the good wettability of hydrogels.

Polysiloxane hydrogels which are water swollen copolymers of 2-hydroxyethyl methacrylate or N-vinyl-pyrrolidone (NVP) with di- or tri-methacrylate functional poly-(dimethylsiloxane) have been described in U.S. Patent No. 4,136,250 for use as a drug delivery matrix, but also for contact lenses. Copolymers of tri-siloxy-hydroxy alkyl methacrylate with HEMA and/or NVP are described in U.S. Patent Nos. 4,139,692 and 4,139,513, and copolymers of C₁-C₄-dialkylacrylamides with oligosiloxanyl-silylalkylmethacrylates are described in U.S. Patent Nos. 4,182,822 and 4,343,927, also for use as oxygen permeable hydrogel contact lenses. U.S. Patent No. 4,711,943 describes essentially similar Si-containing acrylic hydrogels.

Fluorinated hydrogels for use as soft contact lens materials are also known:

U.S. Patent Nos. 4,433,111 and 4,493,910 describe hydrogels and contact lenses obtained by copolymerization of 20-40 mol % substituted or unsubstituted acrylamide or methacrylamide; 25-55 mol % N-vinylpyrrolidone (NVP); 5-20% mol % hydroxyalkyl(meth)-acrylate; 1-10 mol % (meth)-acrylic acid, and 1-9 mol % of a perfluoroalkylalkylene(meth)-acrylate; the perfluoroalkyl groups act to reduce protein deposition.

U.S. Patent No. 4,640,965 describes hydrogels and contact lenses obtained by copolymerisation of hydroxyfluoralkylstyrene (5-60%, by weight), with hydroxyalkyl (meth)-acrylates or N-vinylpyrrolidone (40-95%, by weight); the hydroxy groups are necessary to attain the required compatibility.

U.S. Patent No. 4,638,040 describes the synthesis of 1,3-bis(trifluoroacetoxy)propyl-2-methacrylate polymers and their use as hydrogel-contact lens materials or as ocular implants after hydrolysis.

U.S. Patent No. 4,650,843 describes hydrogel contact lens materials consisting essentially of copolymers of 50-95% (by weight) of 2-hydroxyethyl-methacrylate and 5-35% (by weight) of fluorinated methacrylates with up to 5 F-atoms.

Copolymers of N,N-dimethylacrylamide (DMA) with perfluoroalkylacrylates or methacrylates are described in European patent application 351 364 for use as oxygen permeable hydrogel contact lenses.

In all the cited prior-art is the hydrophilic component based of water-soluble vinyl monomers, like HEMA, NVP or DMA, which are copolymerized with silicone and/or fluorine containing monomers or prepolymers. Although a great variety of Si or F containing hydrogels can be prepared with these hydrophilic monomers, they all possess as hydrophilic component a carbon-carbon backbone polymer; for the specific requirements of long-term in-eye use, contact lenses with poly-(ethylene oxide) (PEO) as hydrophilic component would be preferable since PEO is considered to have better biocompatibility and less lipid and protein adsorption problems. Less protein adsorption generally means less discoloration, better wettability and comfort, and generally a longer uselife for a contact lens.

Poly-(ethylene oxide) as part of a silicone containing hydrogel is included also in U.S. Patent No. 4,136,250, in form of dimethacrylate-(PEO)-(PDMSi)-(PEO) block copolymers, copolymerized with HEMA or NVP; the amount of PEO incorporated into the polymer is limited due to the presence of the other comonomers. Similar poly-(propylene oxide)-PDMSi block copolymers are disclosed in U.S. Patent No. 4,740,533 although this patent is directed toward essentially water free polymers for contact lenses.

Poly-(ethylene oxide) as part of fluorine containing hydrophilic polymers are also described: U.S. Patent No. 3,728,151 describes PEO block copolymer with perfluoroalkyl (-R_f) acrylates and -methacrylates, obtained by chain transfer polymerization with PEO-dithiols; by virtue of their synthesis method these polymers are linear, non-crosslinked, low molecular weight polymers of the A-B-A block type; their use is in textile finishing, where they import anti-soiling and soil-releasing, self-washing properties.

U.S. Patent No. 4,046,944 describes block copolyurethane-ureas prepared from PEO-diols and PEO-diamines, bis-perfluoroalkyl substituted butane diols and diisocyanates, also for use in textile finishing as soil-release agents. This polymer too is not crosslinked and therefore not a hydrogel, and of limited molecular weight.

EP-A-277,771 discloses contact lenses comprising a copolymer of an organosilicone monomer, a fluoroalkyl ester monomer and a hydrophilic monomer, improved by further addition of a linear polysiloxane oligomeric cross-linking agent with or without neopentylglycol dimethacrylate. Polyethers having terminal vinyl groups are not disclosed.

US-A-4,528,301 discloses a contact lens material which is the copolymerization product of a reaction mixture comprising (1) styrene or a ring substituted styrene, (2) a vinyl alcohol ester such as vinyl acetate, (3) a polyethylene glycol ester such as pentaethyleneglycol monomethacrylate, (4) a substituted polysiloxane such as dimethyl polysiloxane or a substituted silane, and, optionally, (5) a cross-linking agent such as divinyl benzene. The polyethylene glycol ester is restricted to monoesters such that polyethers having at least two terminal vinyl groups are not contemplated.

No PEO and F-containing hydrogels are described in the prior art for use in biomaterials and contact lenses. This is probably due to the difficulty in making clear compositions of high molecular weight; since the PEO-hydrophile is a pre-polymeric unit of at least 1,000 MW, the F-containing part of the polymer has to be present in a polymeric form as well; block-copolymers of this type are clear only if the blocks are sufficiently short and association between blocks are in size smaller than the wavelength of light. PEO and F-blocks are especially difficult to combine into a clear copolymer because of the inherent incompatibility of their prepolymeric and monomeric precursors and their very different refraction indices.

It has now unexpectedly been discovered that crosslinked, clear, wettable and highly oxygen permeable poly(ethylene oxide) and fluorine or silicone containing polymers can be prepared, if α,ω -divinyl functionalized PEO-prepolymers are copolymerized with perfluoroalkylacrylates or methacrylates and/or oligosiloxy-silylalkyl acrylates or methacrylates, optionally in the presence either of a third comonomer or a non-reactive solvent or solvent mixture, capable of dissolving all monomeric components.

After synthesis, the polymers can be transformed by equilibration in water into flexible, clear, wettable and oxygen permeable hydrogels, which are useful in biomedical application, as oxygen permeable films and coatings and especially as deposit resistant, highly oxygen permeable contact lenses.

It has further been discovered, that clear block-copolymers with analogous structures can also be made with poly-propylene oxide and poly-tetramethylene oxide as polyether blocks. These block copolymers are strong, flexible, O₂-permeable and, despite a low (< 5%) water content, highly wettable and are therefore useful in many of the abovementioned applications.

The instant invention pertains to copolymers which are oxygen permeable, flexible, wettable, biocompatible and suitable for use in ophthalmic devices, such as contact lenses, which copolymers comprise the polymerization product of

- 55 (A) 10 to 80% by weight of a vinyl-telechelic polyether, or a mixture thereof,
- (B) 90 to 20% by weight of
 - (B-1) a fluorinated, ethylenically unsaturated monomer, or

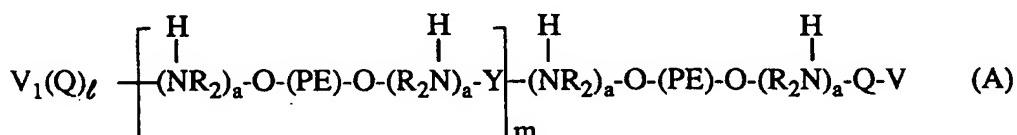
(B-2) a silicone-containing ethylenically unsaturated monomer, or a mixture of monomer (B-1) and monomer (B-2), and

(C) 0 to 60% by weight of an ethylenically unsaturated monomer or mixture of monomers other than monomer (B-1) or monomer (B-2).

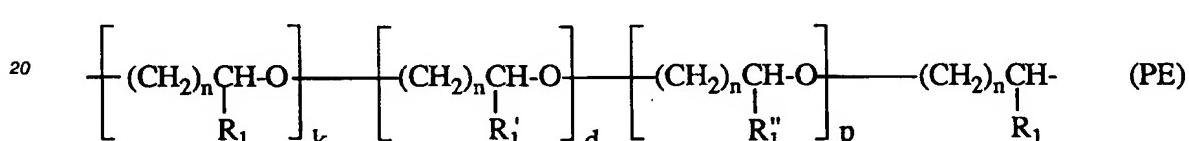
5 Another object of the invention are those copolymers which comprise 20 to 80% by weight of (A) and 80 to 20% by weight of (B) and are otherwise as defined in the preceding paragraph.

Copolymers which are valuable subembodiments of the invention are disclosed in claims 2 to 41.

The vinyl-telechelic polyether (A) preferably has the formula:



15 wherein PE has a number average molecular weight (MW) of about 500 to about 10000 and preferably has the formula:



25 wherein n is 1 to 3,

k, d and p are integers from 0 to 300, and the sum of k + d + p is 7 to 300,

R₁, R_{1'} and R_{1''} are independently of each other hydrogen or methyl, with the proviso that if n is 3, R₁, R_{1'} and R_{1''} are hydrogen, thus describing the backbones of poly(ethylene oxide), poly(propylene oxide) and poly(butylene oxide), but also block-copolymers of the aforementioned alkylene oxides,

30 a is zero or 1,

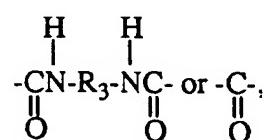
m is an integer from zero to 2,

t is zero or 1,

R₂ is linear or branched alkylene with 2 to 4 carbon atoms;

Y is

35



40

wherein R₃ is a divalent aliphatic group with 2 to 14 carbon atoms, a divalent 5- or 6-membered cycloaliphatic group with 5 to 15 C-atoms, or an arylene group with 6 to 14 C-atoms, with the proviso, that if Y is

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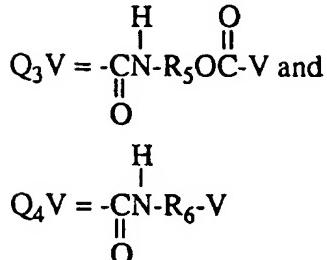
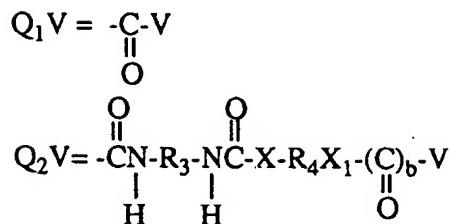


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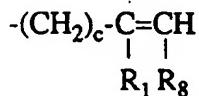
a is 1;

Q is selected from (shown as attached to V):

55.



- 20 wherein R_4 is alkylene of 2 to 4 carbon atoms,
 R_5 is alkylene of 2 to 10 carbon atoms,
 R_6 is arylene or alkyl-substituted arylene of 6 to 20 carbon atoms,
 X is $-O-$ or $-NR_7-$, wherein R_7 is alkyl of 1 to 5 carbon atoms,
 X_1 is $-O-, NH-$ or $-NR_7-$,
25 b is zero or 1,
 V is



- c is zero or 1,
 V_1 has same meaning as V , or is H or R_9 , when t is zero,
35 R_8 is H or $-COOH$, with the proviso that, if R_8 is $-COOH$, R_1 is H, c is zero, and Q is Q_1 ;
 R_9 is alkyl of 1 to 18 carbon atoms;
with the further proviso that when Q is Q_2 , a is zero;
when Q is Q_2 , Q_3 or Q_4 , R_8 is H;
when c is 1, b is zero, Q is Q_2 and R_1 and R_8 are H; and
40 when V_1 is R_9 , m is zero.

The foregoing description for (A) thus includes poly(alkylene oxide) diols and α,ω -diaminoalkyl poly(alkylene oxides) ($a = 1$), of about 500 to about 10000 molecular weight, optionally chain-extended with diisocyanates ($m > 0$) and endcapped either directly with vinyl unsaturated isocyanates, preferably 2-isocyanatoethyl methacrylate (IEM) or m-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI) ($Q = Q_3$ and Q_4); included are also the same poly(alkylene oxides) capped with diisocyanates, followed by reaction with amino- or hydroxy- alkyl acrylates, -methacrylates, -acrylamides or -methacrylamides, hydroxyalkyl vinyl ether or allyl alcohol ($Q = Q_2$); as well as direct ester or amides ($Q = Q_1$).

If less than equivalent molar amounts of capping reactants are used, some of the vinyltelechelic macromers are terminated by vinyl groups only on one end ($V_1 = H$ or R_9).

Thus, the vinyl unsaturated groups are bonded to the poly(alkyleneoxide) chain ends, either directly by ester or amide linkages ($Q = Q_1$); by two urethane or urea linkages and one ester or amide linkage ($Q = Q_2$), or by one urethane or urea and one ester linkage ($Q = Q_3$), or by a urea linkage alone ($Q = Q_4$).

Preferred are poly(alkylene oxide) vinyl unsaturated prepolymers of structures (A) where Q is of structure Q_2 , Q_3 or Q_4 ; most preferred are prepolymers (A) where PE is poly(ethylene oxide), poly(propylene oxide) or poly(ethylene oxide-co-propylene oxide), and Q is of structures Q_3 or Q_4 and a is 1.

Preferred vinyl unsaturated groups V are segments of acrylic, methacrylic and styrenic groups, with methacrylic and styrenic groups being most preferred.

Preferred groups R_3 are the diradical residues of divalent aliphatic diisocyanates with 6-12 carbon atoms, of divalent cycloaliphatic diisocyanates with 6-15 carbon atoms and of divalent aromatic diisocyanates with 6 to 10 carbon atoms.

Most preferred are the diradical residues of isophorone diisocyanate and of 2,4,4(2,2,4)-trimethylhexane-1,6-diisocyanate.

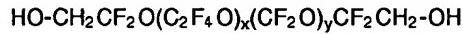
Preferred groups R_5 are ethylene, propylene and butylene, with ethylene being most preferred.

Preferred groups R_6 are phenylene and alpha, alpha-dimethylbenzylene with alpha, alpha-dimethylbenzylene being most preferred.

Useful polyethers PE include: poly-(ethylene oxide) (PEO) diols of 500-10000 MW; poly-(propylene oxide) (PPO) diols of 500-10000 MW; a poly-(ethylene oxide -co-propylene oxide) diol of random or block copolymer structure in ratios of PEO:PPO from 1:30 to 30:1 and with 500-10000 MW; poly-(tetra-methylene oxide) (PTMO) diols with 500-10000 MW.

It is within the scope of the present invention to use not only the di-functional polyethers of structure (A), but also a great variety of tri- or tetrafunctional poly-ether alkanols, as they can be easily prepared by alkoxylation of triols, amines or diamines; tetra-(polyalkylene oxide)-alkanols are for instance known under the tradename TETRONIC (BASF) and are alkylene oxide adducts to ethylene diamine. Also useful are products known as ETHOMEEN (AKZO Chemie) surfactants, which are ethylene oxide adducts to C_{11} - C_{18} alkyl amines. By amination the corresponding tri- or tetra-amines can be prepared, for example, the amination products of propylene oxide adducts to glycerol or trimethylol-propane are available as JEFFAMINE-T from Texaco Chem. Corp. and are also useful in the context of this invention.

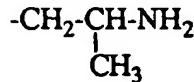
Also useful in the context of this invention are fluorinated polyethers of MW 600-5000, for example:



wherein

x and y are independently of each other integers from 6 to 50, as for instance described in U.S. Patent No. 4,440,918.

Preferred are α,ω -di-(aminopropyl) PEO of 1000-8000 MW; and α,ω -di-(aminopropyl) PPO of 1000-8000 MW and α,ω -di-(aminopropyl)poly-(ethylene oxide-co-propylene oxide) of 1000 to 10000 MW. Most preferred are α,ω -di-(aminopropyl)-PEO and α,ω -di-(aminopropyl)-PPO or α,ω -di-(aminopropyl) (ethylene-co-propylene oxide) of 1000-8000 MW, where the aminopropyl group $-R_2\text{-NH}_2$ is of structure:



These amino terminated poly(alkylene oxides) are prepared, for example by amination of the corresponding diols and are commercially available under the tradename JEFFAMINE from Texaco Chem. Corp.

Diisocyanates of structure $R_3\text{-(NCO)}_2$ useful to form the prepolymer intermediate before capping with a reactive vinyl monomer, are aliphatic, cycloaliphatic or aromatic diisocyanates or mixtures thereof selected from the group consisting of ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatobenzene, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatocyclohexenyl)methane, bis(4-isocyanatophenyl)-methane, 2,6- and 2,4-toluene diisocyanate; 3,3'-dichloro-4,4'-diisocyanatobiphenyl; 1,5-diisocyanatonaphthalene, hydrogenated toluene diisocyanate; 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane (=isophorone diisocyanate); 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate, 2,2'-diisocyanatodiethyl fumarate; 1,5-diisocyanatol-carboxypentane; 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- and 2,3-diisocyanato-naphthalene; 2,4- and 2,7-diisocyanato-1-methylnaphthalene; 4,4'-diisocyanatobiphenyl; 4,4'-diisocyanato-3,3'-diisocyanato-6(7)-methylnaphthalene; 4,4'-diisocyanato-2,2'-dimethyl biphenyl; bis(4-isocyanatophenyl)ethane; and bis(4-isocyanatophenyl) ether.

The preferred diisocyanates are isophorone diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate and 2,4- and 2,6-toluene diisocyanate.

Unsaturated, polymerizable vinyl compounds of structure $V-(\text{CO})_b\text{-X}_1\text{R}_4\text{XH}$ useful to react with the NCO-capped poly-(alkylene oxides) contain hydroxy or amino groups and are selected from the groups consisting of acrylic, methacrylic, acrylamido, methacrylamido, vinyl ether, styrene, allyl, maleate, fumarate and itaconate moieties. Typical examples include: 2-hydroxyethyl acrylate and methacrylate, 2- and 3-hydroxypropyl acrylate and methacrylate; 4-hydroxybutyl acrylate and methacrylate; glycerol

dimethacrylate; hydroxyethyl maleate and fumarate; 2-hydroxyethyl- and 4-hydroxy-butyl vinyl ether; N-tert.-butyl-aminoethyl methacrylate, N-(3-hydroxypropyl)-methacrylamide; vinyl-benzyl alcohol; allyl alcohol.

Preferred active hydrogen containing vinyl compounds are 2-hydroxyethyl acrylate and methacrylate and N-tert.-butyl-aminoethyl methacrylate.

5 Vinyl unsaturated isocyanates of structure V-COOR₆NCO or V-R₆-NCO useful to make the vinyl-telechelic poly-(alkylene oxides) in one step include 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.

Such compounds and their preparation are disclosed, for example, in U.S. Patent No. 2,718,516 and
10 British Patent No. 1,252,099.

Other useful isocyanates include isocyanatoalkyl vinyl ethers, such as 2-isocyanatoethyl vinyl ether, and styrene isocyanate and m-isopropenyl-alpha, alpha- dimethylbenzyl isocyanate. Also useful are isocyanates obtained by the reaction of one mole of a hydroxy- or aminoalkyl acrylate or methacrylate with one mole of a diisocyanate of structure R₃(NCO)₂. Examples of useful such acrylates and methacrylates include 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl methacrylate, or t-butylaminoethyl methacrylate; suitable diisocyanates include isophorone diisocyanate, (3,3,4)-trimethylhexane-1,6-diisocyanate, toluene diisocyanate, diphenylmethane-4,4'-diisocyanate and the like.

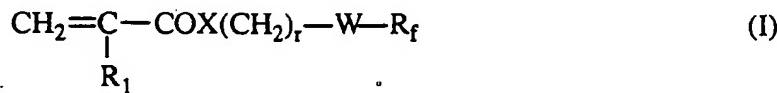
Most preferred are 2-isocyanatoethyl methacrylate and m-isopropenyl- α,α -dimethylbenzyl isocyanate.

Vinyl-telechelic polyethers with Q of structure Q₁ are made, for example, by esterification with acrylic acid, acroyl chloride, acrylic acid anhydride or the methacrylic analog, or by transesterification with methyl acrylate or methacrylate, or by reaction with maleic- or itaconic anhydride or fumaroyl chloride.

The vinyl-telechelic poly-(alkylene oxides) can be used singly or in combination with each other.

The fluorinated and/or silicone containing monomers (B) useful for making the novel polymers of this invention are acrylic or styrenic monomers. Fluorine-containing monomers (B-1) are vinyl monomers containing at least three fluorine atoms selected from the group consisting of hexafluoroisopropyl acrylate and methacrylate, perfluorocyclohexyl acrylate and methacrylate, pentafluorostyrene and the acrylate or methacrylate esters or amides of the formula

30



35 wherein

R_f is -(CF₂)_tCF₂L or -(CF₂CF₂)_qOCF(CF₃)₂

R₁ is hydrogen or methyl,

X is oxygen or -NR₇- wherein R₇ is an alkyl group with 1-5 carbon atoms,

r is an integer from 1-4,

40 t is an integer from 0-14,

q is an integer from 1-3;

L is hydrogen or fluorine, with the proviso that, when t is 0, L is fluorine; and

W is a direct bond or a divalent group of the structure -NR₇-CO-; -NR₇SO₂-(CH₂)_r-; -NR₇SO₂-; -S-(CH₂)_r-; -NR₇-(CH₂)_r-NR₇SO₂-; or -NHCO-.

45 Typical examples are 1,1,2,2-tetrahydroperfluorodecyl acrylate and methacrylate, 1,1,2,2-tetrahydroperfluoroctyl acrylate and methacrylate and 1,1,2,2 tetrahydroperfluoroctyl methacrylamide or acrylamide.

Other useful fluorinated monomers include hexafluoroisopropyl acrylate, hexafluoroisopropyl methacrylate, perfluorocyclohexyl methacrylate, and 2,3,4,5,6-pentafluoro-styrene; the acrylates and methacrylates of fluoroalkyl substituted amido-alcohols, such as of C₇F₁₅CON(C₂H₅)C₂H₄OH; of sulfonamido-alcohols, such as of

C₈F₁₇C₂H₄SO₂N(CH₃)-C₄H₈OH and C₈F₁₇SO₂N(C₂H₅)C₂H₄OH; of perfluoroether alcohols, such as of C₃F₇-O(C₃F₆O)₂CF(CF₃)-CH₂OH or

(CF₃)₂CFO(CF₂CF₂)₂-CH₂CH₂OH; and the acrylates and methacrylates of fluorinated thioether alcohols of structure CF₃(CF₂)₁CH₂CH₂SCH₂CH₂CH₂OH; acrylates and methacrylates of sulfonamido-amines, such as of

55 R_iSO₂N(CH₃)CH₂CH₂N(CH₃)(CH₂)₃NH₂ and R_iCH₂SO₂NH(CH₂)₂NH₂; of amidoamines, such as of R_iCONH(CH₂)₂NH₂; as well as the vinyl monomers obtained by reaction of these aforementioned fluorinated alcohols and amines with 2-isocyanatoethyl acrylate or methacrylate or m-isopropenyl-1,1-dimethylbenzyl

isocyanate.

Preferred are fluorinated monomers in which X is oxygen, W is a direct bond, R₁ is hydrogen, r is 2, t is 6 to 10 and L is fluorine; or in which r is 1 or 2, t is 1-4 and L is fluorine, or in which R₁ is methyl, r is 2, t is 4 to 10 and L is fluorine.

5 Preferred are hexafluoroisopropyl methacrylate, trifluoroethyl methacrylate, and 1,1,2,2-tetrahydroperfluoroctyl and 1,1,2,2-tetrahydroperfluorodecyl acrylate and methacrylate, with 1,1,2,2-tetrahydroperfluoroctyl acrylate being most preferred.

Silicone containing vinyl monomers (B-2) are oligosioxanyl-silylalkyl acrylates and methacrylates containing from 2-10 Si-atoms. Typical representatives include: tris(trimethylsiloxy-silyl)propyl (meth)-
10 acrylate, triphenyldimethyl-disiloxanyl methyl (meth)acrylate, pentamethyl-disiloxanyl methyl acrylate, tert-butyl-tetramethyldisiloxanyl ethyl (meth)acrylate, methyl-di(trimethylsiloxy)silylpropyl-glyceryl (meth)acrylate; pentamethyl-di-siloxanyl-methyl methacrylate; heptamethyl-cyclotetrasiloxyl methyl methacrylate; heptamethyl-cyclotetrasiloxyl-propyl methacrylate; (trimethylsilyl)-decamethyl-pentasiloxy-propyl methacrylate; undecamethyl pentasiloxypropyl methacrylate. Preferably the monomer is tris (trimethylsiloxy-silyl) propyl
15 methacrylate.

The (B-1) fluorine and/or (B-2) silicone containing monomer units as (B) can be present in the polymers of this invention in amounts of 20-90%, preferable 40-80%, most preferably 50-70% by weight. When mixtures of (B-1) and (B-2) are used, they are preferably in a weight ratio of 4:1 to 1:4.

The monomers (C) which can be present in the polymers of this invention in amounts from 0-60% can
20 be any copolymerizable vinyl monomer, like an ester or amide of acrylic or methacrylic acid with from 1-20 carbon atoms in a linear or branched aliphatic, cycloaliphatic or aromatic group containing ester or amide group, and which may be interrupted by hetero atoms like sulfur or oxygen; analogous mono- or di-esters of maleic and itaconic acid; alkyl vinyl ethers with 1 to 10 carbon atoms in the alkyl group, vinyl esters of C₁ to C₁₂- carboxylic acids; styrene and alkyl substituted styrene and α -methylstyrene; hydroxylalkyl acrylates,
25 methacrylates, acrylamides and methacrylamides; alkyl- and dialkyl-amino-alkyl methacrylates and methacrylamides; hydroxylalkyl vinyl ethers, hydroxylalkyl maleates and itaconates.

These comonomers are preferably present in amounts of 5-60%, most preferably in amounts of 10-50% by weight.

Representative examples include: methyl acrylate, ethyl acrylate, n- and isopropyl acrylate, cyclohexyl
30 acrylate, trimethyl-cyclohexyl acrylate, phenyl acrylate, benzyl acrylate and all the corresponding methacrylates; furfuryl acrylate and methacrylate; methoxy-ethyl-, ethoxy-ethyl-, and ethoxy-ethoxy ethyl acrylate and methacrylate; 2-hydroxyethyl acrylate and methacrylate, 3-hydroxypropyl acrylate, methacrylate and methacrylamide; glycidyl methacrylate; N,N-dimethylacrylamide; N-isopropyl- acrylamide; N-vinylacetamide; N-vinyl-pyrrolidone; dimethylamino-ethyl methacrylate and methacrylamide; acrylic and
35 methacrylic acid, vinyl sulfonic acid, 4-styrene sulfonic acid and 2-methacrylamido-2-methyl-propane-sulfonic acid and their salts.

Preferred are methoxy-ethyl acrylate and methoxy-ethyl methacrylate, ethoxy-ethyl acrylate and ethoxy-ethyl methacrylate; methyl methacrylate; methyl acrylate, 2-hydroxyethyl methacrylate; N-vinylpyrrolidone; N,N-dimethyl-acrylamide and styrene, and ethoxy-ethoxy-ethyl acrylate.

40 The vinyl-telechelic poly-alkylene oxides (A) may be prepared, either, most easily, in one step by the reaction of (poly-alkylene oxide) diols or diamines with the halide, anhydride or lower alkyl ester of acrylic, methacrylic, maleic or itaconic acid, or an isocyanatoalkyl acrylate or methacrylate or a styrene isocyanate, or alternatively, in two steps, by reaction with, first, an organic diisocyanate followed by, secondly, reaction with a hydroxy- or amino functional alkyl acrylate, alkyl methacrylate, alkyl maleate, alkyl itaconate, alkyl
45 vinyl ether, allyl compound or styrene. Preferably, the vinyl-telechelic poly-(alkylene oxides) are synthesized by reaction of the poly-(alkylene oxide) diols or diamines with vinyl-unsaturated isocyanates. For urethane bond formation, catalysts are used in amounts from 0.01-0.5%. Typical catalysts include stannous octoate or dibutyltin dilaurate (DBTL), or tert.-amines like triethylamine.

Copolymerization of the vinyl-telechelic poly-(alkylene oxides) (A) with comonomers (B) and (C) may be
50 carried out by employing initiators which generate free-radicals on application of an activating energy as is conventionally used in the polymerization of ethylenically unsaturated monomers. Included among free-radical initiators are the conventional thermally activated initiators such as organic peroxides and organic hydroperoxides. Representative examples of such initiators include benzoyl peroxide, tertiary-butyl perbenzoate, diisopropyl peroxydicarbonate, cumene hydroperoxide, azobis(isobutyronitrile), and the like. Generally, from about 0.01 to 5 percent by weight of thermal initiator is used.

Preferably, UV-initiated polymerization is carried out, using photoinitiators. Such initiators are well known and have been described, for example, in polymerization art, e.g., Chapter II of "Photochemistry" by Calvert and Pitts, John Wiley & Sons (1966). The preferred initiators are photoinitiators which facilitate

polymerization when the composition is irradiated. Representative examples of such initiators include acyloin and derivatives thereof, such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether and α -methylbenzoin; diketones such as benzil and diacetyl, etc.; ketones such as acetophenone, α,α,α -tribromoacetophenone, α,α,α -diethoxyacetophenone (DEAP), 2-hydroxy-2-methyl-1-phenyl-1-propanone, α -nitro- α,α,α -tribromoacetophenone, benzophenone and p,p' -tetramethyldiaminobenzophenone; α -acyloxime esters such as benzil-(O-ethoxycarbonyl)- α -monoxime; ketone/amine combinations such as benzophenone/N-methyldiethanolamine, benzophenone/tributylamine and benzophenone/Michler's ketone; and benzil ketals such as benzil dimethyl ketal, benzil diethyl ketal and 2,5-dichlorobenzil dimethyl ketal. Normally, the photoinitiator is used in amounts ranging from about 0.01 to 5% by weight of the total oligomeric composition.

Preferably, about 0.1 to 1.0% of photoinitiator is used in the polymerizable compositions.

Polymerization may be carried out in bulk in a conventional manner or in the presence of a solvent. Especially in case of poly-(ethylene oxide) as (A) building block, cosolvents are usually required to compatibilize components (A) and (B). The amount of solvent required depends on the nature and relative amounts of (A) and (B), but also on the choice of comonomer (C), which can act as a solvent for (A) and (B). Useful solvents to carry out the polymerization include ketones, like acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone and cyclohexanone; alcohols like ethanol, isopropanol or ethyl-cellulosolve; ethers like ethylene glycol or diethylene glycol dimethyl ether; esters like ethyl acetate or isopropyl acetate; dimethyl sulfoxide; N-methylpyrrolidone; N,N-dimethylformamide; N,N-dimethylacetamide and the like.

The polymerization is carried out in molds, which can consist of plastics, glass or metal and can be any shape. For making films and sheets, the molds are preferably made of glass plates and lined with MYLAR or other polymer films and held together by clamps, using a spacer of desired thickness. Contact lenses are preferably prepared in UV-permeable plastic molds.

After polymerization is complete, the polymer is removed from the mold and any solvent present is either removed by vacuum drying or extraction with water and with water-soluble solvents, or water-solvent mixtures. Useful solvents are acetone, ethanol, methanol, isopropanol and the like. Azeotropic distillation is also a useful procedure to remove certain solvents. After the solvent is removed the polymer is equilibrated in distilled water and its water content is determined gravimetrically. All subsequent measurements are carried out on the water-equilibrated polymers.

In the following examples bending angle is determined on 2.5 x 0.5 inch 1 mm thick, cast sheets by determining the angle formed by a 2 inch overhang and the horizontal. Oxygen permeability is measured with a O₂-Permeometer-Model 201-T (Createch), using buffered saline (pH = 7) as electrolyte and is expressed in units

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$$O_2 \cdot DK (\text{barriers}) = \frac{cm^3(\text{STP})cm \cdot 10^{-10}}{cm^2 \cdot \text{sec} \cdot \text{cmHg}} \quad \text{at a given thickness and temperature}$$

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Physical-mechanical measurements are carried out with an INSTRON testing apparatus, model 1123 on 0.6-1 mm thick sheets.

Water content is expressed as:

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$$\% H_2O = \frac{\text{weight of swollen polymer} - \text{weight of dry polymer}}{\text{weight of swollen polymer}} \times 100$$

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Examples 1-25 describe the synthesis of fluorine or silicone containing poly-(ethylene oxide) block copolymer hydrogels.

Example 1: Synthesis of Poly-(ethylene oxide)-urethane Dimethacrylate

55 120 g (0.0358 m) Polyethylene oxide diol (PEO) of MW 3350 are filled into a 500 ml round bottom flask, equipped with a magnetic stirring bar, gas-inlet tube, thermometer and heating mantle. The PEO is heated to 80°C and the molten resin is stirred for 2 hours at a vacuum of ≤ 0.05 - 1 mm Hg; the liquid is slowly cooled to 50°C and the vacuum broken with dry air. 60 g Isopropyl acetate (IPAC) are added and a clear

solution is formed.

11.18 g (0.072 m) 2-isocyanatoethyl methacrylate and 21.8 g isopropyl acetate are filled into an addition funnel and are slowly added to the PEO solution. 50 g IPAC are used to rinse the funnel. After addition is complete, 0.071 g dibutyl-tin dilaurate (DBTL) (0.15 mol %) are added and the mixture is stirred at 50 °C under dry air for three hours or until all NCO has been consumed as determined by IR-analysis. The product is allowed to cool down and crystallize and 60 g IPAC are added to form a slurry. The slurry is filtered and dried to a white powder, weighing 128.4 g (98% of theory).

Example 2: Using the same procedure as described in example 1, a PEO-di(urethanemethacrylate) is prepared, using poly-(ethylene oxide) diol of 1450 MW.

10 Example 3: Synthesis of Si-containing Poly-(ethylene oxide) Block Copolymers

5 5 g of the PEO-dimethacrylate of example 1 are mixed with 5 g tris-(trimethylsiloxy)-silyl-propyl methacrylate (Si₃MA), 4 g N-methylpyrrolidone (NMP), 6 g methyl ethyl ketone (MEK) and 0.4 % benzoin methyl ether (BME) as UV initiator. The solution is degassed by vacuum which then is broken with dry nitrogen and is filled into a 0.5 mm wide MYLAR lined glass mold held together by clamps, after which it is 15 finally polymerized by exposure to UV radiation from a SYLVANIA Black-Lite Blue lamp for 8 hours.

The clear polymer sheet is removed from the mold and the solvent is exchanged with water first by immersion for 12 hours in distilled water, followed by one hour boiling and equilibration for 48 hours.

A clear, flexible hydrogel is obtained which contains 54.4 % water, has a bending angle of 58° and an oxygen permeability DK of 52 barrers.

20 Example 4: Synthesis of poly-ethylene oxide urea-dimethacrylate from α,ω-di-(1-methyl-aminoethyl) poly-(ethylene oxide).

5 57.68 g (0.020 m) of a α,ω-di(1-methyl-aminoethyl) poly-(ethylene oxide) of MW 2884 and 57.7 g of anhydrous methyl propyl ketone are charged into a 3-neck round bottomed flask which has been equipped with a stirrer, nitrogen inlet, condenser, thermometer and dropping funnel. The solution is stirred at room 25 temperature under dry nitrogen. Then 6.20 g (0.04 mole) of 2-isocyanatoethyl methacrylate (MW 155) dissolved in 6.2 g of anhydrous methylpropyl ketone are added slowly from the dropping funnel. The mildly exothermic reaction is maintained at 35 °C and below by water bath cooling for 1 hour at which time an IR analysis shows the reaction to be complete.

Example 5-13: Following the procedure of example 3, the PEO-urea dimethacrylate of example 4 is

30 mixed with various fluorinated comonomers (F-mon) and other comonomers, using methyl propyl ketone (MPK) as a solvent. 0.5% Benzoin methyl ether is added. The mixtures are degassed, filled into 1 mm thick molds and cured for 8 hours by UV. The polymer sheets are removed from the mold, extracted for 24 hours by swelling in ethanol, boiled for 1 hour in distilled water followed by equilibration in water.

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Composition and test results are shown in the following table.

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Example 5-13

Following the procedure of example 3, fluorine containing PEO-block copolymer hydrogels are synthesized and their properties are determined using the fluorinated monomers and solvent compositions shown in the Table;

Ex. No.	PEO-dimethacrylate of Ex.; %	Si, F-containing comonomer	Other %	Solvents		Properties		
				NMP/MEK %/%	[P] ²⁾ %	H ₂ O %	Bending Angle °	O ₂ /DK (barriers)
5	1	50	R _f A, 50	-	35/65	40	70.0	52
6	1	38	R _f A, 39	MMA 23	40/60	50	49.3	25
7	1	40	Si ₄ MA, 10; R _f A, 30	MMA 20	42/58	51	55.3	55
8	1	30	R _f A, 60	MMA 10	26/74	47	51.6	28
9	2	50	Si ₄ MA, 50	-	70/30	42	44.0	22
10	2	50	R _f A, 50	-	45/55	25	55.1	50
11	1	59	R _f A, 41	-	35/65	37	71.0	43
12	1	50	F ₇ MA, 50	-	50/50	50	57.2	15
13	1	50	F ₆ MA, 50	-	50/50	50	59.7	17

1) R_fA is C_nF_{2n+1}-CH₂CH₂OOC-CH=CH₂, with n = 6/8/10/12 in weight percent of 0.5/75/22/2.5

Si₄MA is tri(trimethylsiloxy-silyl-propyl methacrylate

F₇MA is heptafluorobutyl methacrylate

F₆MA is hexafluoroisopropyl methacrylate

MMA is methyl methacrylate

2) [P] is polymer (monomer) concentration in solvent.

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Example 14: Using the procedure of example 3, selected PEO-block copolymers are synthesized in 1 mm wide MYLAR lined molds and their physical-mechanical properties are measured and reported in the following table.

Polymer of Ex.	H ₂ O %	Tensile Strength Kg/cm ²	Young's Modulus Kg/cm ²	Elongation %
5	3	54.4	6.3	13.6
	6	49.3	33.0	93.4
	11	71.0	4.6	25.0
	12	57.2	25.1	106.0
	13	59.7	16.6	69.4

10 Example 15: The hydrolytic stability of PEO-block copolymers is evaluated by aging in pH 7.4 phosphate-buffered saline solution at 80°C for 132 hours and measuring physical properties before and after aging. The results are shown in the Table.

Polymer of Example		H ₂ O %	Tensile Strength kg/cm ²	Young's Modulus kg/cm ²	Elongation %	Bending Angle °
15	9	initial: aged:	44 43	8.9 7.0	28 26	65 50
	10	initial: aged:	55 56	2.7 3.0	17 17	38 25
20						26 30
						50 50

25 Example 16-25: Following the procedure of example 3, the PEO-urea dimethacrylate of example 4 is mixed with various fluorinated comonomers (F-mon) and other comonomers, using methy-propyl ketone (MPK) as a solvent.. 0.5% Benzoin methyl ether is added. The mixtures are degassed, filled into 1 mm thick molds and cured for 8 hours by UV. The polymer sheets are removed from the mold, extracted for 24 hours by swelling in ethanol, boiled for 1 hour in distilled water followed by equilibration in water.

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Compositions and test results are shown in the following table.

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Example 16-25

Ex. No. of Ex. 4	Macromer	Composition				[Pol]	H ₂ O %	INSTRON Data				O ₂ . DK Barrings at mm/ ^o C
		F-mon %	MMA %	MOEA %	XL %			Bend- ing °	Tensile Strength Kg/cm ²	Young's Modulus Kg/cm ²	Elongation %	
16	40	C ₆ FA 40	20	-	-	57.8	44.7	37	9.3	23.8	117	21 0.4/20
17	30	RfA, 50	20	-	-	55.5	48.8	58	5.3	6.3	274	30 0.4/20
18	30	C ₆ FA 50	20	-	-	67.1	32.7	33	17.8	31.9	253	41 0.1/21
19	30	RfA 50	19.8	-	0.2	56.6	41.1	44	10.8	22.2	242	41 0.1/23
20	30	RfA 60	9.8	-	0.2	50.2	44.2	43	7.6	17.6	87	55 0.1/23
21	30	RfA 60	-	10	0.2	51.8	46.3	49	6.3	14.1	88	33 0.45/20
22	30	RfA 50	-	19.8	0.2	54.1	43.9	38	3.7	12.9	47	45 0.1/23
23	35	RfA 45	-	20	-	54.6	47.9	55	3.1	13.2	34	35 0.99/20
24	40	RfA 40	-	20	-	56.3	51.3	45	2.4	15.5	18	33 0.97/20
25	30	RfA 45	-	25	-	55.7	44.6	55	4.8	10.7	117	35 0.96/22
p-HEMA, for comparison							39.0	60	3.0	5.5	90	6 0.25/22

Abbreviations: MMA = methyl methacrylate
MOEA = methoxy-ethyl acrylate
XL = ethyleneglycol dimethacrylate
RfA = Rf-ethyl acrylate

R_f = C_nF_{2n+1}, n = 6/8/10/12 = 5.4/72.8/20.8/0.9, in % (w/w).
C₆FA = R_fA with n = 6
[PoL] = polymer % in MPK

Examples 26-50 describe the synthesis of silicone and/or fluorine containing poly-(propylene oxide) block copolymers.

Example 26: 41.98 g (0.020 m) α,ω -Bis-(aminopropyl)-poly(propylene oxide) of MW 2099 are charged into a 3-necked round bottomed flask, equipped with stirrer, nitrogen inlet, condenser, thermometer and dropping funnel. The liquid is stirred at room temperature under dry nitrogen while 6.20 g (0.040 m) 2-isocyanatoethyl methacrylate (IEM) are slowly added. The mildly exothermic reaction mixture is maintained at 35° C by water bath cooling for one hour after which time IR analysis shows the reaction to be complete.

5 Example 27: Following the procedure of example 26, a methacrylate terminated poly(propylene oxide) prepolymer is prepared from α,ω -bis-(1-methyl-amino ethyl)-poly(propylene oxide) of MW 4408.

10 Example 28: The procedure of example 26 is repeated, but using m-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI) as the vinyl-unsaturated isocyanate.

15 Example 29: The procedure of example 27 is repeated, but using m-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI) as the vinyl-unsaturated isocyanate.

20 Examples 30-32: Synthesis of chain extended, methacrylate-terminated poly- (propylene oxide).

25 100.75 g (0.048 m) of α,ω -Di-(aminopropyl)-poly-(propylene oxide) of MW 2099 are charged into a 3-necked round bottomed flask which is equipped with a stirrer, nitrogen inlet, condenser, thermometer and dropping funnel. The liquid is stirred at room temperature under dry nitrogen. 1.26 g (0.006 m) 2,2,4(2,4,4) Trimethylhexane- 1,6-diisocyanate (TMDI) are added and the reaction mixture is kept at 28° C for 2 hours, by which time all NCO-groups are reacted, as determined by IR-analysis, yielding a partially chain extended prepolymer containing PPO and TMDI in a mol ratio of 8:1. Then 13.03 g (0.084 m) of 2-isocyanatoethyl methacrylate (IEM) (MW 155) are added slowly from the dropping funnel. The mildly exothermic reaction is maintained at 35° C and below by water bath cooling for 1 hour, at which time an IR analysis shows the reaction to be complete.

30 By the same procedure, chain extended IEM-capped PPO-prepolymers are prepared, containing PPO and TMDI in mol ratios of

35 Example 31: 5/1 (PPO/TMDI)

40 Example 32: 4/1 (PPO/TMDI)

Examples 33-40: Following the procedure of example 3, the poly(propylene oxide)-dimethacrylates of example 26-32 are mixed and reacted with fluorinated comonomers and other comonomers, in the presence of methyl-propyl ketone (MPK) as a solvent; 0.4% benzoin methyl ether (BME) and 8 hours UV-exposure are used for curing. After polymerization, the clear polymer sheets are removed, boiled in water for one hour to strip off unreacted monomer and solvent, and equilibrated in distilled water.

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The polymer compositions thus prepared and their properties are shown in the table.

Example 33-40

Composition

Ex. No.	Macromer of Ex.	F- mon %	M-3 %	[P] %	H ₂ O %	Tensile Strength Kg/cm ²	Young's Modulus Kg/cm ²	Elongation %	O ₂ .DK Barrings, at mm/ ^o C
33	26	40	R _f A 40	DMA 20	69	21.4	3.5	23.5	20
34	26	40	R _f A 40	MMA 20	75	3.1	11.9	30.9	98
35	27	50	C ₈ FA 30	MOEA 20	90	3.2	5.3	9.0	254
36	27	50	C ₆ FA 50	-	80	3.5	8.6	11.0	183
37	32	40	R _f A, 40	MMA 20	75	2.6	25.7	43.3	278
38	27	40	R _f A, 40	MOEA 20	74	2.3	8.0	14.0	122
39	27	40	C ₈ FA 40	MOEA 20	74	2.9	7.2	12.6	175
40	27	40	C ₆ FA 40	EOEMA 20	75	1.9	4.8	6.8	151

R_fA, MMA, MOEA, are as described in example 16.

[P] is as described in example 5

DMA is dimethylacrylamide

C₈FA and C₆FA are R_fA with n = 6 and 8

M-3 are other comonomers

EOEMA is ethoxy-ethyl methacrylate

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Example 41-50: Following the procedure of example 3, the poly(propylene oxide)-dimethacrylates of examples 26, 27 and 28 are mixed and reacted with fluorinated comonomers and other comonomers, but no solvent is used. To the clear mixtures are added 0.2% benzoin methyl ether (BME), and 5 hour UV exposure is used for the polymerization step. After polymerization, the clear polymer sheets are removed from the molds, immersed in boiling water for one hour and equilibrated in distilled water.

The polymer compositions thus prepared and their properties are listed in the table.

Example 41-50

Composition

Ex. No.	Macromer of Ex.	F- mon %	M-3 %	H ₂ O Strength %	Tensile Modulus Kg/cm ²	Young's Modulus Kg/cm ²	Elongation %	O ₂ ,DK Barriers, at mm/ ^o C			
41	28	22.2	R _f A 22.2	MA	55.6	4.4	4.0	11.5	50	42,	0.91/23
42	28	22.3	R _f A 22.2	MOEA	55.6	3.1	8.0	17.6	115	40,	0.90/23
43	28	22.2	R _f A 22.2	EOEA	55.6	3.1	2.6	9.7	33	40,	1.0/23
44	28	25	R _f A 25	EOEMA	50	2.6	4.8	11.9	69	35,	0.95/23
45	26	25	C ₆ FA 25	EOEA	50	2.2	5.3	11.2	78	35,	0.97/22
46	26	25	C ₆ FA 25	EOEMA	50	2.4	8.3	12.7	125	23,	0.95/22
47	27	33	C ₆ FA 33	EOEA	34	2.2	5.5	9.0	123	58,	1/23
48	27	33	C ₆ FA 33	EOEMA	34	2.1	5.3	9.2	129	44,	1/23
49	27	33	C ₆ FA 32	MOEA	36	2.8	4.8	9.2	104	45,	1/23
50	27	31	C ₆ FA 31	EOEOEA	34	3.0	4.6	9.3	86	68,	1/24

R_fA, C₆FA and MOEA are as described in Example 16;

EOEA is ethoxy-ethyl acrylate

EOEMA is ethoxy-ethyl methacrylate

EOEOEA is ethoxy-ethoxy ethyl acrylate

MA is methyl acrylate

Example 51: 99.0 g (0.050 m) Poly-(butylene oxide) diol of MW 1980 are charged into a 3-necked round bottomed flask, equipped with stirrer, nitrogen inlet tube, condenser thermometer and dropping funnel. 0.03 g Dibutyltin dilaurate are added and the solution is stirred at room temperature under dry nitrogen while 16.28 g (0.105 m) 2-isocyanatoethyl methacrylate (IEM) are slowly added. The mildly

exothermic reaction mixture is maintained at 35°C for one hour, after which time IR-analysis shows no free remaining NCO-groups.

A 0.5 mm thick polymer sheet is cast following the procedure of example 3 and having the following composition and properties:

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	poly-butyleneoxide-dimethacrylate	: 25%
	C ₆ F ₁₃ CH ₂ CH ₂ OOC-CH=CH ₂	: 25%
	methoxyethyl acrylate	: 50%

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Physical properties

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Tensile Strength	: 6.8 kg/cm ²
Youngs Modulus	: 16.7 kg/cm ²
Elongation	: 66%
O ₂ .DK	: 13 barrers (0.4 mm/20°C)

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Water absorption is 1.4%

Example 52: 428.0 g (0.2223 m) Poly-(butylene oxide) diol of MW 1925 are charged into a 3-necked round bottomed flask, equipped with stirrer, nitrogen inlet tube, condenser thermometer and dropping funnel. 0.050 g Dibutyltin dilaurate are added and the liquid is stirred at room temperature under dry nitrogen while 98.7 g (0.447 m) isophorone diisocyanate (IPDI) are slowly added. The mildly exothermic reaction mixture is maintained at 35°C for 1 1/3 hour, after which time NCO-titration shows the free remaining NCO-groups to be one half of their original concentration. 60.3 g (0.463 m) 2-Hydroxyethyl methacrylate are added to the reaction mixture which is then stirred at 30-35°C for 22 hours, after which time no free NCO can be detected by IR analysis.

A 0.5 mm thick polymer sheet is cast following the procedure of example 3 and having the following composition and properties:

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	poly-butyleneoxide-dimethacrylate	: 33%
	C ₆ F ₁₃ CH ₂ CH ₂ OOC-CH=CH ₂	: 33%
	methoxyethyl acrylate	: 34%

Physical properties

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Tensile Strength	: 6.9 kg/cm ²
Youngs Modulus	: 14.7 kg/cm ²
Elongation	: 74%
O ₂ .DK	: 20 barrers (0.4 mm/20°C)

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Water absorption is 1.8%

Example 53 and 54: Synthesis of PEO-di-(urea-methacrylate) copolymers with R₁-ethyl acrylate or tris(trimethyloxy)-silyl-propyl methacrylate.

59.95 g (0.010 m) α,ω -Di(1-methyl-aminoethyl) poly-(ethylene oxide) of MW 5995 and 59.95 g of anhydrous methyl propyl ketone are charged into a 3-necked round bottomed flask equipped with a stirrer, nitrogen inlet, condenser, thermometer and dropping funnel. The solution is stirred at room temperature under dry nitrogen. Then 3.10 g (0.020 mole) of 2-isocyanatoethyl methacrylate (MW 155) dissolved in 3.1 g of anhydrous methyl propyl ketone are added slowly from the dropping funnel. The mildly exothermic reaction is maintained at 35°C and below by water bath cooling for 1 hour at which time IR analysis shows the reaction to be complete.

Following the procedure of example 3, the PEO-dimethacrylate is reacted with a fluorinated and a silicone containing comonomer, using methyl-propyl ketone as a solvent. The clear polymer sheets are worked up as described and tested (C₆FA is C₁₆F₁₃-ethylacrylate; Si₄MA is tris-(trimethylsiloxy)-silylpropyl methacrylate; [POL] is concentration of monomer/polymer in methyl propyl ketone).

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10	Ex.	Composition %					INSTRON Data					
		No.	Macromer	C ₆ FA	Si ₄ MA	MOEA	[POL] %	H ₂ O Strength %	Tensile Modulus Kg/cm ²	Young's Modulus Kg/cm ²	Elongation %	O ₂ .DK Barrers, at mm/ [°] C
								%	Kg/cm ²	Kg/cm ²	%	at mm/ [°] C
15		53	30	50	-	20	70	51.3	2.3	3.1	119	51 0.5/20
		54	40	-	40	20	63	57.7	3.3	3.3	227	47 0.5/20

C₆FA, Si₄MA, MOEA, [POL] are defined in example 5 and 16

20

Example 55: Synthesis of PEO (MW ~ 6000) di(urea-alpha-methyl styrene)

59.95 g (0.010 m) of α,ω -Di-(1-methyl-aminoethyl)-poly-(ethylene oxide) of MW 5995 (Jeffamine-ED 6000) and 59.95 g of anhydrous methyl propyl ketone are charged into a 3-necked round bottomed flask which 25 has been equipped with a stirrer, nitrogen inlet, condenser, thermometer and dropping funnel. The solution is stirred at room temperature under dry nitrogen, then 4.02 g (0.020 mole) of m-isopropenyl-alpha,alpha-diamethylbenzyl isocyanate (MW 201) dissolved in 3.1 g of anhydrous methylpropyl ketone are added slowly from the dropping funnel. The mildly exothermic reaction is maintained at 35 °C and below by water bath cooling for 1 hour, at which time an IR analysis shows the reaction to be complete.

30 Example 56-59: Following the general procedure of example 3, but using 25% methyl-propyl ketone as solvent, and using the PEO-macromers of example 53 and 55, fluorinated copolymer hydrogels are prepared and their properties measured.

35	Ex.	Macromer	C ₆ FA %	M-3 %	H ₂ O Tensile Strength %					Young's Modulus Kg/cm ²	Elongation %	O ₂ .DK Barrers, at mm/ [°] C
					No. of Ex.	%	%	%	Kg/cm ²	Kg/cm ²		
40	56	53	40	40	MOMA	20	58.0	4.8	3.9	298	41	0.5/17
	57	53	40	40	MOA	20	58.2	2.3	4.2	70	42	0.5/17
45	58	55	40	40	MOMA	20	61.6	2.4	1.8	261	40	0.5/17
	59	55	40	40	MOA	20	60.5	3.7	5.9	102	41	0.5/17



MOMA is methoxy-ethyl methacrylate

MOA is methoxy-ethyl acrylate

55

Example 60: The macromer-monomer mixtures of examples 16, 56, 57, 58, and 59 are filled into polypropylene contact lens molds, which are exposed to UV radiation from a SYLVANIA Blacklite-blue lamp for four hours. The molds are opened and the lenses are released during equilibration in distilled water. Clear,

soft and wettable contact lenses are obtained.

Example 61: Using the same procedure as described in example 60, contact lenses are prepared from the PPO-macromer/monomer solutions of example 45 and 47. Clear, soft contact lenses are obtained.

Example 62-67: Using the procedure described in example 3, the following compositions are prepared and their water content and physical properties are determined.

Compositions

10 Example No.	Mac of Ex.	Mac %	C ₆ FA %	H ₂ O %	O ₂ -DK barbers at mm/ ^o C	Tensile Strength Kg/cm ²	Young's Modulus Kg/cm ²	Elongation %
15 62	4	30	70	34.8	39 0.5 /22	4.0	7.1	160
63	4+53 ¹⁾	30	70	44.9	43 0.43/20	5.2	7.3	190
20 64	53	30	70	51.8	51 0.5 /20	2.3	3.9	220
65	4	20	80	28.3	48 0.43/22	4.6	9.4	200
25 66	4+53 ¹⁾	20	80	36.6	43 0.45/22	7.4	4.9	380
67	53	20	80	41.1	53 0.45/20	3.8	2.4	490

All polymers form clear, flexible hydrogels in water.

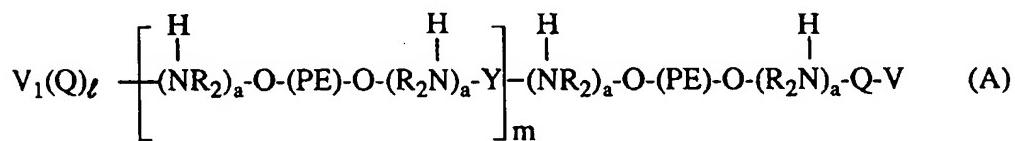
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1) Equal parts, by weight.

35 **Claims**

Claims for the following Contracting States : AT, BE, CH, LI, DE, DK, FR, GB, GR, IT, LU, NL, SE

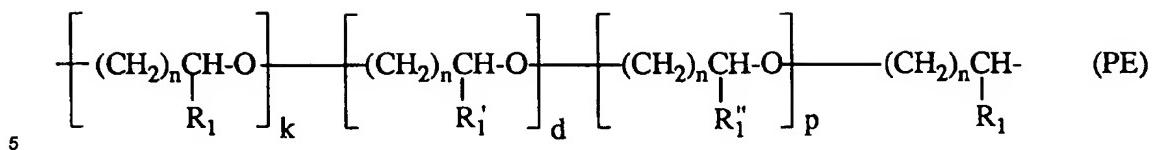
1. A copolymer which is oxygen permeable, flexible, wettable, biocompatible and suitable for use in ophthalmic devices, such as contact lenses, which copolymer comprises the polymerization product of
 - (A) 10 to 80% by weight of a vinyl-telechelic polyether, or a mixture thereof,
 - (B) 90 to 20% by weight of
 - (B-1) a fluorinated, ethylenically unsaturated monomer, or
 - (B-2) a silicone-containing ethylenically unsaturated monomer, or a mixture of monomer (B-1) and monomer (B-2), and
 - (C) 0 to 60% by weight of an ethylenically unsaturated monomer or mixture of monomers other than monomer (B-1) or monomer (B-2).
2. A copolymer according to claim 1 wherein the vinyl-telechelic polyether (A) has the formula (A):

50



55

wherein PE has a number average molecular weight (MW) of about 500 to about 10000 and has the formula:



wherein n is 1 to 3,

k, d and p are integers from 0 to 300, and the sum of k + d + p is 7 to 300,

R₁, R_{1'} and R_{1''} are independently of each other hydrogen or methyl, with the proviso that if n is 3, R₁,

10 R_{1'} and R_{1''} are hydrogen,

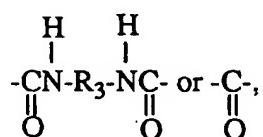
a is zero or 1,

m is an integer from zero to 2,

t is zero or 1,

R₂ is linear or branched alkylene with 2 to 4 carbon atoms;

15 Y is

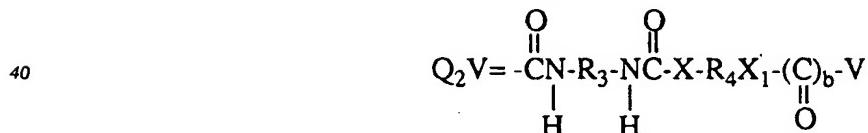


wherein R₃ is a divalent aliphatic group with 2 to 14 carbon atoms, a divalent 5- or 6-membered cycloaliphatic group with 5 to 15 C-atoms, or an arylene group with 6 to 14 C-atoms, with the proviso, that if Y is



a is 1;

Q is selected from (shown as attached to V):



wherein R₄ is alkylene of 2 to 4 carbon atoms,

55 R₅ is alkylene of 2 to 10 carbon atoms,

R₆ is arylene or alkyl-substituted arylene of 6 to 20 carbon atoms,

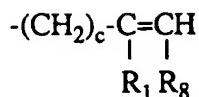
X is -O- or -NR₇- , wherein R₇ is alkyl of 1 to 5 carbon atoms,

X₁ is -O-, -NH- or -NR₇- ,

b is zero or 1,

V is

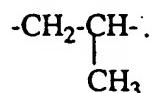
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c is zero or 1,

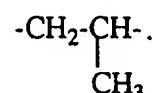
- 10 V₁ has same meaning as V, or is H or R₉, when t is zero,
 R₈ is H or -COOH, with the proviso that, if R₈ is -COOH, R₁ is H, c is zero, and Q is Q₁;
 R₉ is alkyl of 1 to 18 carbon atoms;
 with the further proviso that
 when Q is Q₂, a is zero;
 15 when Q is Q₂, Q₃ or Q₄, R₈ is H;
 when c is 1, b is zero, Q is Q₂ and R₁ and R₈ are H; and
 when V₁ is R₉, m is zero.
3. A copolymer according to claim 2 wherein the polyether PE is a poly(ethylene oxide) (PEO) of 500-
 20 10000 MW, a poly(propylene oxide) (PPO) of 500-10000 MW, a poly(ethylene oxide-co-propylene
 oxide) of random or block copolymer structure in ratios of PEO:PPO from 1:30 to 30:1 of 500-10000
 MW, or a poly(tetramethylene oxide) of 500-10000 MW.
4. A copolymer according to claim 3 wherein the polyether PE is a poly(ethylene oxide) of 1000-8000
 25 MW, or a poly(ethylene oxide-co-propylene oxide) of 1000-10000 MW and wherein a is 1 and R₂ is

30



5. A copolymer according to claim 3 wherein the polyether is an poly(propylene oxide) of 1000-8000 MW,
 a is 1 and R₂ is

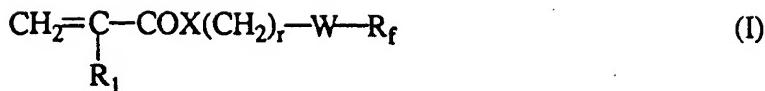
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6. A copolymer according to claim 3 wherein QV is Q₂V, wherein in Q₂ R₃ is a divalent radical obtained
 by removing the two -NCO groups from a diisocyanate selected from the group consisting of ethylene
 diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,2-
 45 diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatobenzene, bis(4-
 isocyanatocyclohexyl)methane, bis(4-isocyanatocyclohexenyl)methane, bis(4-isocyanatophenyl)-meth-
 ane, 2,6- and 2,4-toluene diisocyanate; 3,3'-dichloro-4,4'-diisocyanatobiphenyl; 1,5-diisocyanatonaph-
 thalene, hydrogenated toluene diisocyanate; 1-isocyanatomethyl-5-isocyanato-1,3, 3-trimethylcyclohex-
 ane (=isophorone diisocyanate); 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate, 2,2'-
 50 diisocyanatodiethyl fumarate; 1,5-diisocyanato-1-carboxypentane; 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- and
 2,3-diisocyanatonaphthalene; 2,4- and 2,7-diisocyanato-1-methylnaphthalene; 4,4'-diisocyanatobiphenyl;
 4,4'-diisocyanato-3,3'-diisocyanato-6(7)-methylnaphthalene; 4,4'-diisocyanato-2,2'-dimethyl biphenyl;
 bis(4-isocyanatophenyl) ethane; and bis(4-isocyanatophenyl) ether, and V-(CO)_b-X₁-R₄-X- is the radical
 obtained by removing the active hydrogen atom from a hydroxyl or amino group of a compound
 55 selected from the group consisting of 2-hydroxyethyl acrylate and methacrylate, 2- and 3-hydroxy-
 ypropyl acrylate and methacrylate; 4-hydroxybutyl acrylate and méthacrylate; glycerol dimethacrylate;
 hydroxyethyl maleate and fumarate; 2-hydroxyethyl- and 4-hydroxy-butyl vinyl ether; N-tert.-butyl-
 aminoethyl methacrylate, N-(3-hydroxypropyl)-methacrylamide; vinyl-benzyl alcohol; and allyl alcohol.

7. A copolymer according to claim 6 wherein diisocyanate is isophorone diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate, 2,4-toluene diisocyanate or 2,6-toluene diisocyanate, and the active hydrogen containing vinyl compound is 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate or N-tert-butyl-amino ethyl methacrylate.
- 5 8. A copolymer according to claim 3 wherein QV is $Q_3 V$ and $V-COO-R_5-$ is the radical obtained by removing the -NCO group from an isocyanate compound selected from the group consisting of 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.
- 10 9. A copolymer according to claim 8 wherein the isocyanate compound is 2-isocyanatoethyl methacrylate.
- 10 10. A copolymer according to claim 3 wherein QV is $Q_4 V$ and $V-R_6-$ is the radical obtained by removing the -NCO group from 2-isocyanatobutyl vinyl ether, styrene isocyanate, or m-isopropenyl-alpha,alpha-dimethylbenzyl isocyanate.
- 15 11. A copolymer according to claim 10 wherein the isocyanate is m-isopropenyl-alpha, alpha-dimethylbenzyl isocyanate.
- 20 12. A copolymer according to claim 4 wherein QV is $Q_3 V$ and $V-COO-R_5-$ is the radical obtained by removing the -NCO group from an isocyanate compound selected from the group consisting of 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.
- 25 13. A copolymer according to claim 4 wherein QV is $Q_4 V$ and $V-R_6-$ is the radical obtained by removing the -NCO group from 2-isocyanatobutyl vinyl ether, styrene isocyanate, or m-isopropenyl-alpha,alpha-dimethylbenzyl isocyanate.
- 30 14. A copolymer according to claim 5 wherein QV is $Q_3 V$ and $V-COO-R_5-$ is the radical obtained by removing the -NCO group from an isocyanate compound selected from the group consisting of 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.
- 35 15. A copolymer according to claim 5 wherein QV is $Q_4 V$ and $V-R_6-$ is the radical obtained by removing the -NCO group from 2-isocyanatobutyl vinyl ether, styrene isocyanate, or m-isopropenyl-alpha,alpha-dimethylbenzyl isocyanate.
- 40 16. A copolymer according to claim 12, wherein the isocyanate compound is 2-isocyanatoethyl methacrylate.
- 45 17. A copolymer according to claim 13, wherein the isocyanate is m-isopropenyl-alpha, alpha-dimethylbenzyl isocyanate.
18. A copolymer according to claim 14, wherein the isocyanate is 2-isocyanatoethyl methacrylate.
- 45 19. A copolymer according to claim 15, wherein the isocyanate is m-isopropenyl-alpha, alpha-dimethylbenzyl isocyanate.
- 50 20. A copolymer according to claim 2 wherein PE is poly(ethylene oxide), poly(propylene oxide) or poly(ethylene oxide-co-propylene oxide) and QV is $Q_2 V$, $Q_3 V$ or $Q_4 V$.
21. A copolymer according to claim 20 wherein QV is $Q_3 V$ or $Q_4 V$ and a is 1.
- 55 22. A copolymer according to claim 1 wherein (B-1) is a fluorine containing monomer containing at least three fluorine atoms selected from the group consisting of hexafluoroisopropyl acrylate and methacrylate, perfluorocyclohexyl acrylate and methacrylate, pentafluorostyrene and the acrylate or methacrylate esters or amides of the formula



5

wherein

 R_f is $-(\text{CF}_2)_t\text{CF}_2\text{L}$ or $-(\text{CF}_2\text{CF}_2)_q\text{OCF}(\text{CF}_3)_2$, R_1 is hydrogen or methyl,10 X is oxygen or $-\text{NR}_7-$ wherein R_7 is an alkyl group with 1-5 carbon atoms,

r is an integer from 1-4,

t is an integer from 0-14,

q is an integer from 1-3;

L is hydrogen or fluorine, with the proviso that, when t is 0, L is fluorine; and

15 W is a direct bond or a divalent group of the structure $-\text{NR}_7-\text{CO}-$; $-\text{NR}_7\text{SO}_2-(\text{CH}_2)_r-$; $-\text{NR}_7\text{SO}_2-$; $-\text{S}-(\text{CH}_2)_r-$; $-\text{NR}_7-(\text{CH}_2)_r\text{NR}_7\text{SO}_2-$; or $-\text{NHCO}-$.

23. A copolymer according to claim 1 wherein (B-1) is a fluorinated monomer selected from the group consisting of hexafluoroisopropyl acrylate, hexafluoroisopropyl methacrylate or a compound of structure (I), as defined in claim 22, wherein W is a direct bond and L is fluorine.
24. A copolymer according to claim 22 wherein X is oxygen, W is a direct bond, R_1 is hydrogen, r is 2, t is 6 to 10 and L is fluorine; or in which r is 1 or 2, t is 1-4 and L is fluorine, or in which R_1 is methyl, r is 2, t is 4 to 10 and L is fluorine.

25

25. A copolymer according to claim 22 wherein r is 1 or 2, t is 1 to 4 and L is fluorine.
26. A copolymer according to claim 22 wherein R is methyl, r is 2 and t is 4 to 10 and L is fluorine.
- 30 27. A copolymer according to claim 1 wherein (B-2) is a silicone-containing vinyl monomer which is an oligosiloxanyl-silyl-alkyl acrylate or methacrylate containing 2 to 10 silicon atoms.
- 35 28. A copolymer according to claim 27 wherein the monomer is selected from the group consisting of tris(trimethylsiloxy)-silyl-propyl (meth)acrylate, triphenyldimethyl-disiloxanyl-methyl (meth)acrylate, pentamethyl-disiloxanyl-methyl acrylate, tert-butyltetramethyldisiloxanyl-ethyl (meth)acrylate, methyl-di(trimethylsiloxy)silylpropyl-glyceryl (meth)acrylate; pentamethyldi-siloxanyl-methyl methacrylate; heptamethyl-cyclotetrasiloxy methyl methacrylate; heptamethyl-cyclotetrasiloxy-propyl methacrylate; (trimethylsilyl)-decamethyl-pentasiloxy-propyl methacrylate; and undecamethyl pentasiloxypropyl methacrylate.

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29. A copolymer according to claim 28 wherein the monomer is tris(trimethylsiloxy)-silyl-propyl methacrylate.
30. A copolymer according to claim 1 wherein component (B) is 40 to 80% by weight of said copolymer.

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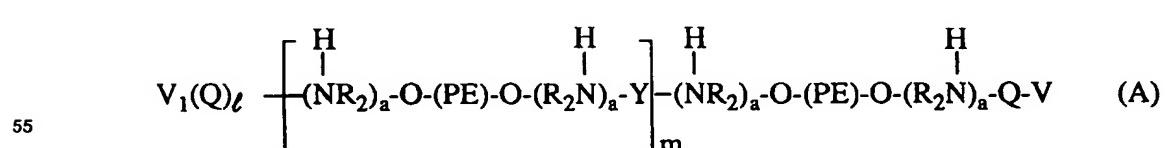
31. A copolymer according to claim 30 wherein component (B) is 50 to 70% by weight of said copolymer.

32. A copolymer according to claim 1 wherein component (C) is a monomer selected from the group consisting of methyl acrylate, ethyl acrylate, n- and isopropyl acrylate, cyclohexyl acrylate, trimethyl-cyclohexyl acrylate, phenyl acrylate, benzyl acrylate and the corresponding methacrylates; furfuryl acrylate and methacrylate; methoxy-ethyl-, ethoxy-ethyl-, and ethoxy-ethoxy ethyl acrylate and methacrylate; 2-hydroxyethyl acrylate and methacrylate, 3-hydroxypropyl acrylate, methacrylate and methacrylamide; glycidyl methacrylate; N,N-dimethylacrylamide; N-isopropyl- acrylamide; N-vinylacetamide; N-vinylpyrrolidone; dimethylamino-ethyl methacrylate and methacrylamide; acrylic and methacrylic acid, vinyl sulfonic acid, styrene, 4-styrene sulfonic acid and 2-methacrylamido-2-methyl-propane-sulfonic acid and their salts, and mixtures thereof.

33. A copolymer according to claim 32 wherein monomer is methoxy-ethyl acrylate and methoxy-ethyl methacrylate, ethoxy-ethyl acrylate and ethoxy-ethyl methacrylate; methyl methacrylate; methyl acrylate, 2-hydroxyethyl methacrylate; N-vinylpyrrolidone; N,N-dimethyl-acrylamide and styrene, and ethoxy-ethoxy-ethyl acrylate or mixtures thereof.
- 5 34. A copolymer according to claim 1 wherein component (C) is 5 to 60% by weight of said copolymer.
35. A copolymer according to claim 34 wherein component (C) is 10 to 50% by weight of said copolymer.
- 10 36. A copolymer according to claim 1 which is in the shape of a contact lens.
37. A copolymer according to claim 1 wherein polyether PE is a fluorinated polyether of MW 600-5000 of structure HO-CH₂CF₂(C₂F₄O)_x(CF₂O)_yCF₂CH₂-OH, wherein x and y are independently of each other integers from 6 to 50.
- 15 38. A copolymer according to claim 4 wherein the amount of component (C) is zero.
39. A copolymer according to claim 4 wherein component (A) is 15-30% by weight of said copolymer.
- 20 40. A copolymer according to claim 5 wherein component (A) is 30-60% by weight of said copolymer.
41. A copolymer according to claim 38 which is in the shape of a contact lens.
- 25 42. A process for the manufacture of a copolymer according to claim 1 characterized in conventionally copolymerizing the monomer mixture by employing initiators which generate free-radicals on application of an activating energy.
43. Use of a copolymer according to claim 1 for the manufacture of a contact lens.
- 30 44. A contact lens comprising a copolymer as defined in claim 1.
45. A contact lens consisting essentially of a copolymer as defined in claim 1.

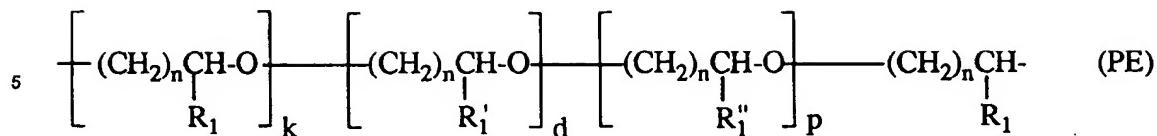
Claims for the following Contracting State : ES

- 35 1. A process for the manufacture of a copolymer which is oxygen permeable, flexible, wettable, biocompatible and suitable for use in ophthalmic devices, such as contact lenses, which copolymer comprises the polymerization product of
- 40 (A) 10 to 80% by weight of a vinyl-telechelic polyether, or a mixture thereof,
- 40 (B) 90 to 20% by weight of
- 45 (B-1) a fluorinated, ethylenically unsaturated monomer, or
- (B-2) a silicone-containing ethylenically unsaturated monomer, or a mixture of monomer (B-1) and monomer (B-2), and
- 45 (C) 0 to 60% by weight of an ethylenically unsaturated monomer or mixture of monomers other than monomer (B-1) or monomer (B-2),
- characterized in conventionally copolymerizing the monomer mixture by employing initiators which generate free-radicals on application of an activating energy.
- 50 2. A process according to claim 1 wherein the vinyl-telechelic polyether (A) has the formula (A):



wherein PE has a number average molecular weight (MW) of about 500 to about 10000 and has the

formula:



wherein n is 1 to 3,

10 k, d and p are integers from 0 to 300, and the sum of k + d + p is 7 to 300,

R_1 , R_1' and R_1'' are independently of each other hydrogen or methyl, with the proviso that if n is 3, R_1 , R_1' and R_1'' are hydrogen,

a is zero or 1,

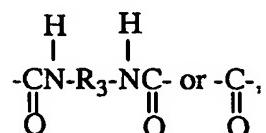
m is an integer from zero to 2,

15 t is zero or 1,

R_2 is linear or branched alkylene with 2 to 4 carbon atoms;

Y is

20



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wherein R_3 is a divalent aliphatic group with 2 to 14 carbon atoms, a divalent 5- or 6-membered cycloaliphatic group with 5 to 15 C-atoms, or an arylene group with 6 to 14 C-atoms, with the proviso, that if Y is

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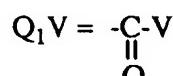


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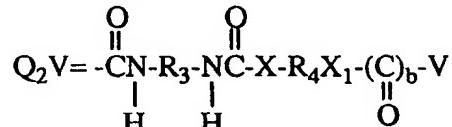
a is 1;

Q is selected from (shown as attached to V):

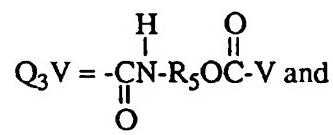
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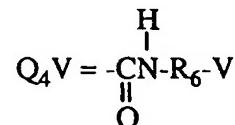
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wherein R_4 is alkylene of 2 to 4 carbon atoms,

R_5 is alkylene of 2 to 10 carbon atoms,

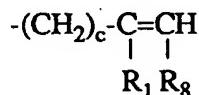
R₆ is arylene or alkyl-substituted arylene of 6 to 20 carbon atoms,

X is -O- or -NR₇-, wherein R₇ is alkyl of 1 to 5 carbon atoms,

X₁ is -O-, -NH- or -NR₇-,

b is zero or 1,

5 V is



10

c is zero or 1,

V₁ has same meaning as V, or is H or R₉, when t is zero,

R₈ is H or -COOH, with the proviso that, if R₈ is -COOH, R₁ is H, c is zero, and Q is Q₁;

15 R₉ is alkyl of 1 to 18 carbon atoms;

with the further proviso that

when Q is Q₂, a is zero;

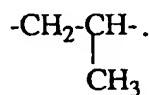
when Q is Q₂, Q₃ or Q₄, R₈ is H;

when c is 1, b is zero, Q is Q₂ and R₁ and R₈ are H; and

20 when V₁ is R₉, m is zero.

3. A process according to claim 2 wherein the polyether PE is a poly(ethylene oxide) (PEO) of 500-10000 MW, a poly(propylene oxide) (PPO) of 500-10000 MW, a poly(ethylene oxide-co-propylene oxide) of random or block copolymer structure in ratios of PEO:PPO from 1:30 to 30:1 of 500-10000 MW, or a poly(tetramethylene oxide) of 500-10000 MW.
- 25
4. A process according to claim 3 wherein the polyether PE is a poly(ethylene oxide) of 1000-8000 MW, or a poly(ethylene oxide-co-propylene oxide) of 1000-10000 MW and wherein a is 1 and R₂ is

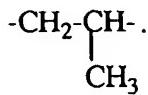
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5. A process according to claim 3 wherein the polyether is an poly(propylene oxide) of 1000-8000 MW, a is 1 and R₂ is

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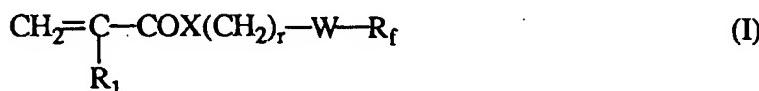
- 45 6. A process according to claim 3 wherein QV is Q₂V, wherein in Q₂ R₃ is a divalent radical obtained by removing the two -NCO groups from a diisocyanate selected from the group consisting of ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatobenzene, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatocyclohexenyl)methane, bis(4-isocyanatophenyl)-methane, 2,6- and 2,4-toluene diisocyanate; 3,3'-dichloro-4,4'-diisocyanatobiphenyl; 1,5-diisocyanatonaphthalene, hydrogenated toluene diisocyanate; 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane (=isophorone diisocyanate); 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate, 2,2'-diisocyanatodiethyl fumarate; 1,5-diisocyanato-1-carboxypentane; 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- and 2,3-diisocyanatonaphthalene; 2,4- and 2,7-diisocyanato-1-methylnaphthalene; 4,4'-diisocyanatobiphenyl; 4,4'-diisocyanato-3,3'-diisocyanato-6(7)-methylnaphthalene; 4,4'-diisocyanato-2,2'-dimethyl biphenyl; bis(4-isocyanatophenyl) ethane; and bis(4-isocyanatophenyl) ether, and V-(CO)_b-X₁-R₄-X- is the radical obtained by removing the active hydrogen atom from a hydroxyl or amino group of a compound selected from the group consisting of 2-hydroxyethyl acrylate and methacrylate, 2- and 3-hydrox-

ypropyl acrylate and methacrylate; 4-hydroxybutyl acrylate and methacrylate; glycerol dimethacrylate; hydroxyethyl maleate and fumarate; 2-hydroxyethyl- and 4-hydroxy-butyl vinyl ether; N-tert.-butyl-aminoethyl methacrylate, N-(3-hydroxypropyl)-methacrylamide; vinyl-benzyl alcohol; and allyl alcohol.

- 5 7. A process according to claim 6 wherein diisocyanate is isophorone diisocyanate, 2,2,4-(2,4,4)-trimethylhexane-1,6-diisocyanate, 2,4-toluene diisocyanate or 2,6-toluene diisocyanate, and the active hydrogen containing vinyl compound is 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate or N-tert. butyl-aminoethyl methacrylate.
- 10 8. A process according to claim 3 wherein QV is $Q_3 V$ and $V-COO-R_5-$ is the radical obtained by removing the -NCO group from an isocyanate compound selected from the group consisting of 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.
- 15 9. A process according to claim 8 wherein the isocyanate compound is 2-isocyanatoethyl methacrylate.
- 20 10. A process according to claim 3 wherein QV is $Q_4 V$ and $V-R_6-$ is the radical obtained by removing the -NCO group from 2-isocyanatobutyl vinyl ether, styrene isocyanate, or m-isopropenyl-alpha, alpha-dimethylbenzyl isocyanate.
- 25 11. A process according to claim 10 wherein the isocyanate is m-isopropenyl-alpha, alpha-dimethylbenzyl isocyanate.
- 30 12. A process according to claim 4 wherein QV is $Q_3 V$ and $V-COO-R_5-$ is the radical obtained by removing the -NCO group from an isocyanate compound selected from the group consisting of 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.
- 35 13. A process according to claim 4 wherein QV is $Q_4 V$ and $V-R_6-$ is the radical obtained by removing the -NCO group from 2-isocyanatobutyl vinyl ether, styrene isocyanate, or m-isopropenyl-alpha, alpha-dimethylbenzyl isocyanate.
- 40 14. A process according to claim 5 wherein QV is $Q_3 V$ and $V-COO-R_5-$ is the radical obtained by removing the -NCO group from an isocyanate compound selected from the group consisting of 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.
- 45 15. A process according to claim 5 wherein QV is $Q_4 V$ and $V-R_6-$ is the radical obtained by removing the -NCO group from 2-isocyanatobutyl vinyl ether, styrene isocyanate, or m-isopropenyl-alpha, alpha-dimethylbenzyl isocyanate.
- 50 16. A process according to claim 12, wherein the isocyanate compound is 2-isocyanatoethyl methacrylate.
- 55 17. A process according to claim 13, wherein the isocyanate is m-isopropenyl-alpha, alpha-dimethyl benzyl isocyanate.
- 60 18. A process according to claim 14, wherein the isocyanate is 2-isocyanatoethyl methacrylate.
- 65 19. A process according to claim 15, wherein the isocyanate is m-isopropenyl-alpha, alpha-dimethyl benzyl isocyanate.
- 70 20. A process according to claim 2 wherein PE is poly(ethylene oxide), poly(propylene oxide) or poly(ethylene oxide-co-propylene oxide) and QV is $Q_2 V$, $Q_3 V$ or $Q_4 V$.
- 75 21. A process according to claim 20 wherein QV is Q_3 or $Q_4 V$ and a is 1.
- 80 22. A process according to claim 1 wherein (B-1) is a fluorine containing monomer containing at least three fluorine atoms selected from the group consisting of hexafluoroisopropyl acrylate and methacrylate,

perfluorocyclohexyl acrylate and methacrylate, pentafluorostyrene and the acrylate or methacrylate esters or amides of the formula

5



10

wherein

R_f is $-(\text{CF}_2)_n\text{CF}_2\text{L}$ or $-(\text{CF}_2\text{CF}_2)_q\text{OCF}(\text{CF}_3)_2$,

R_1 is hydrogen or methyl,

X is oxygen or $-\text{NR}_7-$ wherein R_7 is an alkyl group with 1-5 carbon atoms,

r is an integer from 1-4,

15

t is an integer from 0-14,

q is an integer from 1-3;

L is hydrogen or fluorine, with the proviso that, when t is 0, L is fluorine; and

W is a direct bond or a divalent group of the structure $-\text{NR}_7-\text{CO}-$; $-\text{NR}_7\text{SO}_2-(\text{CH}_2)_r-$; $-\text{NR}_7\text{SO}_2-$; $-\text{S}-(\text{CH}_2)_r-$; $-\text{NR}_7-(\text{CH}_2)_r-\text{NR}_7\text{SO}_2-$; or $-\text{NHCO}-$.

20

23. A process according to claim 1 wherein (B-1) is a fluorinated monomer selected from the group consisting of hexafluoroisopropyl acrylate, hexafluoroisopropyl methacrylate or a compound of structure (I), as defined in claim 22, wherein W is a direct bond and L is fluorine.

25

24. A process according to claim 22 wherein X is oxygen, W is a direct bond, R_1 is hydrogen, r is 2, t is 6 to 10 and L is fluorine; or in which r is 1 or 2, t is 1-4 and L is fluorine, or in which R_1 is methyl, r is 2, t is 4 to 10 and L is fluorine.

25. A process according to claim 22 wherein r is 1 or 2, t is 1 to 4 and L is fluorine.

30

26. A process according to claim 22 wherein R is methyl, r is 2 and t is 4 to 10 and L is fluorine.

27. A process according to claim 1 wherein (B-2) is a silicone-containing vinyl monomer which is an oligosiloxanyl-silyl-alkyl acrylate or methacrylate containing 2 to 10 silicon atoms.

35

28. A process according to claim 27 wherein the monomer is selected from the group consisting of tris(trimethylsiloxy)silyl-propyl (meth)acrylate, triphenyldimethyl-disiloxanymethyl (meth)acrylate, pentamethyl-disiloxanymethyl acrylate, tert-butyltetramethyldisiloxanyethyl (meth)acrylate, methyl-di(trimethylsiloxy)silylpropyl-glyceryl (meth)acrylate; pentamethyldi-siloxanyl-methyl methacrylate; heptamethyl-cyclotetrasiloxy methyl methacrylate; heptarnethyl-cyclotetrasiloxy-propyl methacrylate; (trimethylsilyl)-decamethyl-pentasiloxo-propyl methacrylate; and undecamethyl pentasiloxo-propyl methacrylate.

45

29. A process according to claim 28 wherein the monomer is tris(trimethylsiloxy)silyl-propyl methacrylate.

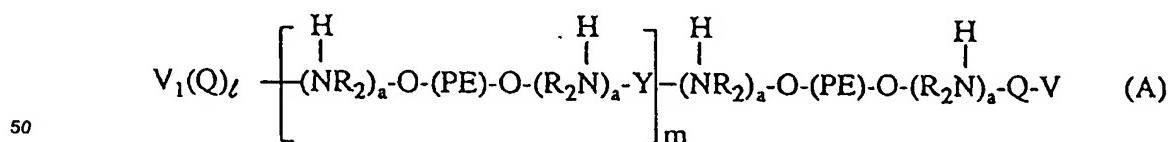
30. A process according to claim 1 wherein component (B) is 40 to 80% by weight of said copolymer.

31. A process according to claim 30 wherein component (B) is 50 to 70% by weight of said copolymer.

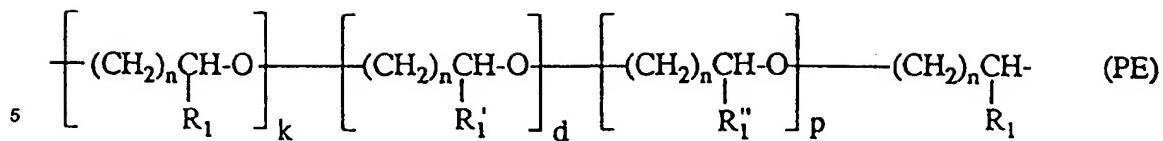
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32. A process according to claim 1 wherein component (C) is a monomer selected from the group consisting of methyl acrylate, ethyl acrylate, n- and isopropyl acrylate, cyclohexyl acrylate, trimethylcyclohexyl acrylate, phenyl acrylate, benzyl acrylate and the corresponding methacrylates; furfuryl acrylate and methacrylate; methoxy-ethyl-, ethoxy-ethyl-, and ethoxy-ethoxy ethyl acrylate and methacrylate; 2-hydroxyethyl acrylate and methacrylate, 3-hydroxypropyl acrylate, methacrylate and methacrylamide; glycidyl methacrylate; N,N-dimethylacrylamide; N-isopropyl- acrylamide; N-vinylacetamide; N-vinylpyrrolidone; dimethylamino-ethyl methacrylate and methacrylamide; acrylic and methacrylic acid, vinyl sulfonic acid, styrene, 4-styrene sulfonic acid and 2-methacrylamido-2-methyl-propane-sulfonic acid and their salts, and mixtures thereof.

33. A process according to claim 32 wherein monomer is methoxy-ethyl acrylate and methoxy-ethyl methacrylate, ethoxy-ethyl acrylate and ethoxy-ethyl methacrylate; methyl methacrylate; methyl acrylate, 2-hydroxyethyl methacrylate; N-vinylpyrrolidone; N,N-dimethyl-acrylamide and styrene, and ethoxy-ethoxy-ethyl acrylate or mixtures thereof.
- 5 34. A process according to claim 1 wherein component (C) is 5 to 60% by weight of said copolymer.
35. A process according to claim 34 wherein component (C) is 10 to 50% by weight of said copolymer.
- 10 36. A process according to claim 1 for the manufacture of a contact lens.
37. A process according to claim 1 wherein polyether PE is a fluorinated polyether of MW 600-5000 of structure HO-CH₂CF₂(C₂F₄O)_x(CF₂O)_yCF₂CH₂-OH, wherein x and y are independently of each other integers from 6 to 50.
- 15 38. A process according to claim 4 wherein the amount of component (C) is zero.
39. A process according to claim 4 wherein component (A) is 15-30% by weight of said copolymer.
- 20 40. A process according to claim 5 wherein component (A) is 30-60% by weight of said copolymer.
41. A process according to claim 38 for the manufacture of a contact lens.
42. Use of a copolymer according to claim 1 for the manufacture of a contact lens.
- 25 43. A contact lens comprising a copolymer as defined in claim 1.
44. A contact lens consisting essentially of a copolymer as defined in claim 1.
- 30 **Patentansprüche**
Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, LI, DE, DK, FR, GB, GR, IT, LU, NL, SE
1. Copolymeres, das sauerstoffdurchlässig, elastisch, benetzbar, biokompatibel und zur Verwendung in ophthalmologischen Vorrichtungen, wie Kontaktlinsen, geeignet ist, dadurch gekennzeichnet, daß es das Polymerisationsprodukt aus
- 35 (A) 10 bis 80 Gew.-% eines Vinyl-telechelen Polyethers oder eines Gemisches daraus,
(B) 90 bis 20 Gew.-% aus
(B-1) einem fluorierten, ethylenisch ungesättigten Monomeren, oder
(B-2) einem Silicon-enthaltenden ethylenisch ungesättigten Monomeren oder einem Gemisch aus
40 Monomer (B-1) und Monomer (B-2), und
(C) 0 bis 60 Gew.-% eines ethylenisch ungesättigten Monomeren oder eines Gemisches der Monomeren, ausgenommen Monomeres (B-1) oder Monomeres (B-2), umfaßt.
- 45 2. Copolymeres nach Anspruch 1, worin der Vinyltelechelene Polyether (A) die Formel (A) besitzt:



worin PE ein zahlendurchschnittliches Molekulargewicht (MG) von etwa 500 bis etwa 10.000 besitzt und die Formel



besitzt, worin n den Wert 1 bis 3 besitzt.

k, d und p ganze Zahlen von 0 bis 300 sind, und die Summe aus $k + d + p$ 7 bis 300 beträgt,

10 R_1 , R_1' und R_1'' unabhängig voneinander für ein Wasserstoffatom oder eine Methylgruppe stehen, mit der Maßgabe, daß wenn n den Wert 3 hat, R_1 , R_1' und R_1'' Wasserstoff bedeuten,

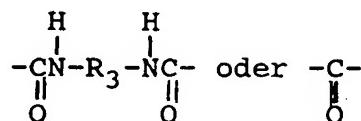
a den Wert 0 oder 1 besitzt

m eine ganze Zahl von 0 bis 2 ist,

ℓ den Wert 0 oder 1 besitzt,

15 R₂ eine lineares oder verzweigtes Alkylen mit 2 bis 4 Kohlenstoffatomen ist,

Y

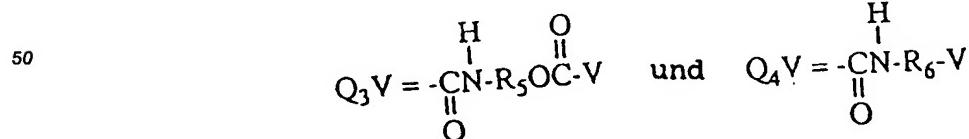
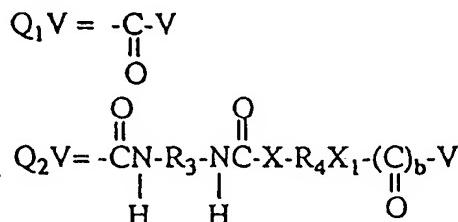


25 bedeutet, worin R₃ eine zweiwertige aliphatische Gruppe mit 2 bis 14 Kohlenstoffatomen, eine zweiwertige 5- oder 6-gliedrige cycloaliphatische Gruppe mit 5 bis 15 Kohlenstoffatomen oder eine Arylengruppe mit 6 bis 14 Kohlenstoffatomen ist, mit der Maßgabe, daß, wenn Y



ist, a den Wert 1 hat:

35 Q ausgewählt ist aus (gezeigt in Bindung an V):



55 worin R₄ ein Alkylen mit 2 bis 4 Kohlenstoffatomen ist,

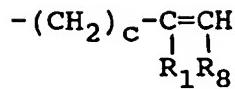
R_5 ein Alkylen mit 2 bis 10 Kohlenstoffatomen ist,

R₆ ein Arylen oder ein Alkyl-substituiertes Arylen mit 6 bis 20 Kohlenstoffatomen ist,

X -O- oder -NR₇- bedeutet, worin R₇ ein Alkyl mit 1 bis 5 Kohlenstoffatomen ist,

X₁ -O-, -NH- oder -NR₇- bedeutet,
b den Wert 0 oder 1 besitzt,
V

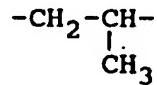
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- 10 bedeutet,
c den Wert 0 oder 1 besitzt,
V₁ die gleiche Bedeutung wie V besitzt, oder für H oder R₉ steht, wenn t den Wert 0 hat,
R₈ für H oder -COOH steht, mit der Maßgabe, daß, wenn R₈ -COOH ist, R₁ H, c 0 und Q Q₁ bedeutet,
R₉ ein Alkyl mit 1 bis 18 Kohlenstoffatomen ist;
15 mit der weiteren Maßgabe, daß, wenn Q Q₂ ist, a für 0 steht;
wenn Q Q₂, Q₃ oder Q₄ ist, R₈ für H steht;
wenn c 1 bedeutet, b 0 ist, Q Q₂ ist und R₁ und R₈ H bedeuten; und
wenn V₁ R₉ ist, m den Wert 0 hat.

- 20 3. Copolymeres nach Anspruch 2, worin der Polyether PE ein Poly(ethylenoxid) (PEO) mit einem Molekulargewicht von 500 bis 10.000, ein Poly(propylenoxid) (PPO) mit einem Molekulargewicht von 500 bis 10.000, ein Poly(ethylenoxidcopropylenoxid) mit einer Zufalls- oder Blockcopolymerstruktur in den Verhältnissen von PEO:PPO von 1:30 bis 30:1 mit einem Molekulargewicht von 500 bis 10.000 oder ein Poly(tetramethylenoxid) mit einem Molekulargewicht von 500 bis 10.000 ist.
25 4. Copolymeres nach Anspruch 3, worin der Polyether PE ein Poly(ethylenoxid) mit einem Molekulargewicht von 1000 bis 8000 oder ein Poly(ethylenoxidcopropylenoxid) mit einem Molekulargewicht von 1000 bis 10.000 ist, und worin a den Wert 1 und R₂

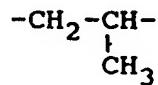
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- 35 bedeutet.

5. Copolymeres nach Anspruch 3, worin der Polyether ein Poly(propylenoxid) mit einem Molekulargewicht von 1000 bis 8000 ist, a den Wert 1 hat und R₂ für

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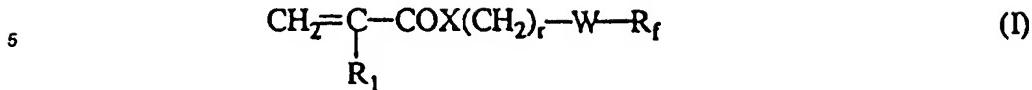


- 45 steht.

6. Copolymeres nach Anspruch 3, worin QV Q₂V ist, worin in Q₂ R₃ ein zweiwertiger Rest ist, erhalten durch Entfernen der zwei NCO-Gruppen aus einem Diisocyanat, ausgewählt aus der Gruppe bestehend aus Ethylendiisocyanat, 1,2-Diisocyanatopropan, 1,3-Diisocyanatopropan, 1,6-Diisocyanatohexan, 1,2-Diisocyanatocyclohexan, 1,3-Diisocyanatocyclohexan, 1,4-Diisocyanatobenzol, Bis-(4-isocyanatocyclohexyl)methan, Bis-(4-isocyanatocyclohexenyl)methan, Bis-(4-isocyanatophenyl)methan, 2,6- und 2,4-Toluoldiisocyanat; 3,3'-Dichlor-4,4'-diisocyanatobiphenyl; 1,5-Diisocyanatonaphthalin, hydriertem Toluoldiisocyanat; 1-Isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexan (=Isophorondiisocyanat); 2,2,4-(2,4,4)-Trimethylhexan-1,6-diisocyanat, 2,2'-Diisocyanatodiethylfumarat; 1,5-Diisocyanato-1-carboxypentan; 1,2, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- und 2,3-Diisocyanatonaphthalin; 2,4- und 2,7-Diisocyanato-1-methyl-naphthalin; 4,4'-Diisocyanatobi-phenyl; 4,4'-Diisocyanato-3,3'-diisocyanato-6(7)-methyl-naphthalin; 4,4'-Diisocyanato-2,2'-dimethylbiphenyl; Bis-(4-isocyanatophenyl)ethan; und Bis-(4-isocyanato-phenyl)ether, und V-(CO)_b-X₁-R₄-X- der Rest, erhalten durch Entfernen des aktiven Wasserstoffatoms aus einer

- Hydroxyl- oder Aminogruppe einer Verbindung, ausgewählt aus der Gruppe, bestehend aus 2-Hydroxyethylacrylat und -methacrylat, 2- und 3-Hydroxypropylacrylat und -methacrylat; 4-Hydroxybutylacrylat und -methacrylat; Glycerindimethacrylat; Hydroxyethylmaleat und -fumarat; 2-Hydroxyethyl- und 4-Hydroxybutylvinylether; N-tert.-Butylaminoethylmethacrylat, N-(3-Hydroxypropyl)methacrylamid; Vinylbenzylalkohol; und Allylalkohol, ist.
7. Copolymeres nach Anspruch 6, worin das Diisocyanat Isophorondiisocyanat, 2,2,4-(2,4,4)-Trimethylhexan-1,6-diisocyanat, 2,4-Toluoldiisocyanat oder 2,6-Toluoldiisocyanat ist, und die den aktiven Wasserstoff enthaltende Vinylverbindung 2-Hydroxyethylmethacrylat, 2-Hydroxyethylacrylat oder N-tert.-Butylaminoethylmethacrylat ist.
8. Copolymeres nach Anspruch 3, worin QV Q₃V ist, und V-COO-R₅- der Rest, erhalten durch Entfernen der NCO-Gruppe von einer Isocyanatverbindung, ausgewählt aus der Gruppe, bestehend aus 2-Isocyanatoethylmethacrylat, 2-Isocyanatoethylacrylat, 3-Isocyanatopropylmethacrylat, 1-Methyl-2-isocyanatoethylmethacrylat, und 1,1-Dimethyl-2-isocyanatoethylacrylat, ist.
9. Copolymeres nach Anspruch 8, worin die Isocyanatverbindung 2-Isocyanatoethylmethacrylat ist.
10. Copolymeres nach Anspruch 3, worin QV Q₄V ist, und V-R₆- der Rest, erhalten durch Entfernen der NCO-Gruppe aus 2-Isocyanatobutylvinylether, Styrolisocyanat oder m-Isopropenyl- α,α -dimethylbenzylisocyanat, ist.
11. Copolymeres nach Anspruch 10, worin das Isocyanat m-Isopropenyl- α,α -dimethylbenzylisocyanat ist.
12. Copolymeres nach Anspruch 4, worin QV Q₃V ist, und V-COO-R₅- der Rest, erhalten durch Entfernen der NCO-Gruppe von einer Isocyanatverbindung, ausgewählt aus der Gruppe, bestehend aus 2-Isocyanatoethylmethacrylat, 2-Isocyanatoethylacrylat, 3-Isocyanatopropylmethacrylat, 1-Methyl-2-isocyanatoethylmethacrylat, und 1,1-Dimethyl-2-isocyanatoethylacrylat, ist.
13. Copolymeres nach Anspruch 4, worin QV Q₄V ist, und V-R₆- der Rest, erhalten durch Entfernen der NCO-Gruppe von 2-Isocyanatobutylvinylether, Styrolisocyanat, oder m-Isopropenyl- α,α -dimethylbenzylisocyanat, ist.
14. Copolymeres nach Anspruch 5, worin QV Q₃V ist, und V-COO-R₅- der Rest, erhalten durch Entfernen der NCO-Gruppe von einer Isocyanatverbindung, ausgewählt aus der Gruppe, bestehend aus 2-Isocyanatoethylmethacrylat, 2-Isocyanatoethylacrylat, 3-Isocyanatopropylmethacrylat, 1-Methyl-2-isocyanatoethylmethacrylat und 1,1-Dimethyl-2-isocyanatoethylacrylat, ist.
15. Copolymeres nach Anspruch 5, worin QV Q₄V ist und V-R₆- der Rest, erhalten durch Entfernen der NCO-Gruppe aus 2-Isocyanatobutylvinylether, Styrolisocyanat oder m-Isopropenyl- α,α -dimethylbenzylisocyanat, ist.
16. Copolymeres nach Anspruch 12, worin die Isocyanatverbindung 2-Isocyanatoethylmethacrylat ist.
17. Copolymeres nach Anspruch 13, worin das Isocyanat m-Isopropenyl- α,α -dimethylbenzylisocyanat ist.
18. Copolymeres nach Anspruch 14, worin das Isocyanat 2-Isocyanatoethylmethacrylat ist.
19. Copolymeres nach Anspruch 15, worin das Isocyanat m-Isopropenyl- α,α -dimethylbenzylisocyanat ist.
20. Copolymeres nach Anspruch 2, worin das PE Poly-(ethylenoxid), Poly-(propylenoxid) oder Poly(ethylen-copropylenoxid) ist, und QV Q₂V, Q₃V oder Q₄V ist.
21. Copolymeres nach Anspruch 20, worin QV Q₃V oder Q₄V bedeutet, und a den Wert 1 hat.
22. Copolymeres nach Anspruch 1, worin (B-1) ein Fluor-enthaltendes Monomeres ist, das mindestens 3 Fluoratome enthält, ausgewählt aus der Gruppe, bestehend aus Hexafluorisopropylacrylat und -methacrylat, Perfluorcyclohexylacrylat und -methacrylat, Pentafluorstyrol und den Acrylat- oder Methacrylate-

stern oder Amiden der Formel



worin

- 10 R_f $-(\text{CF}_2)_q\text{CF}_2\text{L}$ oder $-(\text{CF}_2\text{CF}_2)_q\text{OCF}(\text{CF}_3)_2$ bedeutet,
- 11 R_1 für ein Wasserstoffatom oder eine Methylgruppe steht,
- 12 X für ein Sauerstoffatom oder $-\text{NR}_7-$ steht, worin R_7 eine Alkylgruppe mit 1-5 Kohlenstoffatomen bedeutet,
- 13 r eine ganze Zahl von 1-4 ist,
- 14 t eine ganze Zahl von 0-14 ist,
- 15 q eine ganze Zahl von 1-3 ist;
- 16 L für ein Wasserstoff- oder ein Fluoratom steht, mit der Maßgabe, daß, wenn t den Wert 0 hat, L für ein Fluoratom steht; und W eine direkte Bindung oder eine zweiwertige Gruppe der Struktur $-\text{NR}_7\text{-CO-}$; $\text{NR}_7\text{SO}_2\text{-(CH}_2\text{)}_r\text{-}$; $-\text{NR}_7\text{SO}_2\text{-S-(CH}_2\text{)}_r\text{-}$; $-\text{NR}_7\text{-(CH}_2\text{)}_r\text{-NR}_7\text{SO}_2\text{-}$, oder $-\text{NHCO-}$ ist.

20 23. Copolymeres nach Anspruch 1, worin (B-1) ein fluoriertes Monomeres, ausgewählt aus der Gruppe, bestehend aus Hexafluorisopropylacrylat, Hexafluorisopropylmethacrylat oder eine Verbindung der Struktur (I), wie in Anspruch 22 definiert, worin W eine direkte Bindung und L ein Fluoratom ist, ist.

25 24. Copolymeres nach Anspruch 22, worin X ein Sauerstoffatom ist, W eine direkte Bindung ist, R_1 ein Wasserstoffatom ist, r den Wert 2 besitzt, t den Wert 6 bis 10 besitzt, und L ein Fluoratom ist; oder worin r den Wert 1 oder 2 besitzt, t den Wert 1 bis 4 besitzt und L ein Fluoratom ist, oder worin R_1 eine Methylgruppe bedeutet, r den Wert 2 besitzt, t den Wert 4 bis 10 besitzt und L ein Fluoratom ist.

30 25. Copolymeres nach Anspruch 22, worin r den Wert 1 oder 2 besitzt, t den Wert 1 bis 4 besitzt und L ein Fluoratom ist.

26. Copolymeres nach Anspruch 22, worin R für eine Methylgruppe steht, r den Wert 2 besitzt und t den Wert 4 bis 10 besitzt und L ein Fluoratom bedeutet.

35 27. Copolymeres nach Anspruch 1, worin (B-2) ein Silicon-enthaltendes Vinylmonomeres ist, das ein Oligosiloxanlysilylalkylacrylat oder -methacrylat mit 2 bis 10 Siliciumatomen ist.

40 28. Copolymeres nach Anspruch 27, worin das Monomere aus der Gruppe, bestehend aus Tris(trimethylsiloxy)silylpropyl(meth)acrylat, Triphenyldimethyldisiloxanyl methyl(meth)acrylat, Pentamethyl-disiloxanyl methylacrylat, tert.-Butyltetramethyldisiloxanyethyl(meth)acrylat, Methyldi(trimethylsiloxy)-silylpropylglyceryl(meth)acrylat; Pentamethyldisiloxanyl methylmethacrylat; Heptamethylcyclotetrasilox-ymethylmethacrylat; Heptamethylcyclotetrasiloxypyropylmethacrylat; (Trimethylsilyl)-decamethylpentasiloxypropylmethacrylat; und Undecamethylpentasiloxypropylmethacrylat, ist.

45 29. Copolymeres nach Anspruch 28, worin das Monomere Tris(trimethylsiloxy)silylpropylmethacrylat ist.

30. Copolymeres nach Anspruch 1, worin die Komponente (B) 40 bis 80 Gew.-% des Copolymeren ausmacht.

50 31. Copolymeres nach Anspruch 30, worin die Komponente (B) 50 bis 70 Gew.-% des Copolymeren ausmacht.

55 32. Copolymeres nach Anspruch 1, worin die Komponente (C) ein Monomeres, ausgewählt aus der Gruppe, bestehend aus Methylacrylat, Ethylacrylat, n- und Isopropylacrylat, Cyclohexylacrylat, Trimethylcyclohexylacrylat, Phenylacrylat, Benzylacrylat und den entsprechenden Methacrylaten; Furfurylacrylat und -methacrylat; Methoxyethyl-, Ethoxyethyl- und Ethoxyethoxyethylacrylat und -methacrylat; 2-Hydroxyethylacrylat und -methacrylat; 3-Hydroxypropylacrylat, -methacrylat und -methacrylamid;

Glycidylmethacrylat; N,N-Dimethylacrylamid; N-Isopropylacrylamid; N-Vinylacetamid; N-Vinylpyrrolidon; Dimethylaminoethylmethacrylat und -methacrylamid; Acryl- und Methacrylsäure, Vinylsulfonsäure, Styrol, 4-Styrolsulfonsäure und 2-Methacrylamido-2-methylpropansulfonsäure und ihren Salzen und Gemischen davon, ist.

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33. Copolymeres nach Anspruch 32, worin das Monomere Methoxyethylmethacrylat und Methoxyethylmethacrylat, Ethoxyethylacrylat und Ethoxyethylmethacrylat; Methylmethacrylat; Methylacrylat, 2-Hydroxyethylmethacrylat; N-Vinylpyrrolidon; N,N-Dimethylacrylamid und Styrol, und Ethoxyethoxyethylmethacrylat oder Gemische davon ist.

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34. Copolymeres nach Anspruch 1, worin die Komponente (C) 5 bis 60 Gew.-% des Copolymeren ausmacht.

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35. Copolymeres nach Anspruch 34, worin die Komponente (C) 10 bis 50 Gew.-% des Copolymeren ausmacht.

36. Copolymeres nach Anspruch 1, welches in Form einer Kontaktlinse vorliegt.

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37. Copolymeres nach Anspruch 1, worin der Polyether PE ein fluorierter Polyether mit einem Molekulargewicht von 600 bis 5000 der Struktur HO-CH₂CF₂(C₂F₄O)_x(CF₂O)_y CF₂CH₂-OH, worin x und y unabhängig voneinander ganze Zahlen von 6 bis 50 sind, ist.

38. Copolymeres nach Anspruch 4, worin die Menge der Komponente (C) 0 beträgt.

25

39. Copolymeres nach Anspruch 4, worin die Komponente (A) 15 bis 30 Gew.-% des Copolymeren beträgt.

40. Copolymeres nach Anspruch 5, worin die Komponente (A) 30 bis 60 Gew.-% des Copolymeren beträgt.

41. Copolymeres nach Anspruch 38, welches in Form einer Kontaktlinse vorliegt.

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42. Verfahren zur Herstellung eines Copolymeren nach Anspruch 1, dadurch gekennzeichnet, daß man in an sich bekannter Weise das Monomerengemisch unter Verwendung von Startern, die freie Radikale bei Anwendung einer Aktivierungsenergie erzeugen, copolymerisiert.

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43. Verwendung eines Copolymeren nach Anspruch 1 zur Herstellung einer Kontaktlinse.

44. Kontaktlinse, umfassend ein Copolymeres nach Anspruch 1.

45. Kontaktlinse, bestehend im wesentlichen aus einem Copolymeren nach Anspruch 1.

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Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung eines Copolymeren, das sauerstoffdurchlässig, elastisch, benetzbar, biokompatibel und zur Verwendung in ophthalmologischen Vorrichtungen, wie Kontaktlinsen, geeignet ist, welches das Polymerisationsprodukt von

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- (A) 10 bis 80 Gew.-% eines Vinyl-telechelen Polyethers oder eines Gemisches daraus,

- (B) 90 bis 20 Gew.-% aus

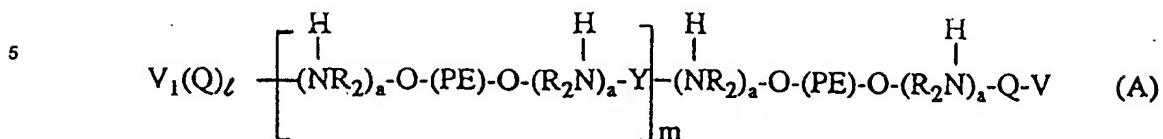
- (B-1) einem fluorierten, ethylenisch ungesättigten Monomeren, oder

- (B-2) einem Silicon-enthaltenden ethylenisch ungesättigten Monomeren oder einem Gemisch aus Monomer (B-1) und Monomer (B-2), und

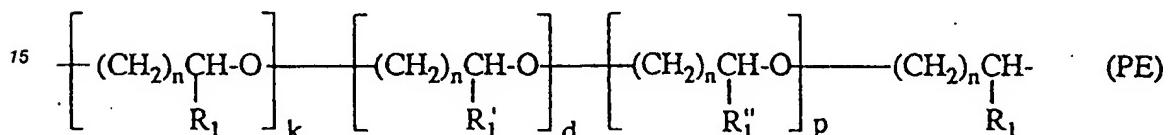
- (C) 0 bis 60 Gew.-% eines ethylenisch ungesättigten Monomeren oder eines Gemisches der Monomeren, ausgenommen Monomeres (B-1) oder Monomeres (B-2), umfaßt, dadurch gekennzeichnet, daß man in an sich bekannter Weise das Monomerengemisch unter Verwendung von Startern, die bei Anwendung einer Aktivierungsenergie freie Radikale erzeugen, copolymerisiert.

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2. Verfahren nach Anspruch 1, worin der Vinyl-telechels Polyether (A) die Formel (A) besitzt:



10 worin PE ein zahlendurchschnittliches Molekulargewicht (MG) von etwa 500 bis etwa 10.000 besitzt und die Formel



20 besitzt, worin n den Wert 1 bis 3 besitzt,

k, d und p ganze Zahlen von 0 bis 300 sind, und die Summe aus k + d + p 7 bis 300 beträgt,
R₁, R_{1'} und R_{1''} unabhängig voneinander für ein Wasserstoffatom oder eine Methylgruppe stehen, mit der Maßgabe, daß wenn n den Wert 3 hat, R₁, R_{1'} und R_{1''} Wasserstoff bedeuten,

a den Wert 0 oder 1 besitzt,

25 m eine ganze Zahl von 0 bis 2 ist,

ℓ den Wert 0 oder 1 besitzt,

R₂ eine lineares oder verzweigtes Alkylen mit 2 bis 4 Kohlenstoffatomen ist, Y



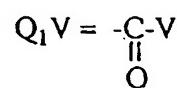
35 bedeutet, worin R₃ eine zweiwertige aliphatische Gruppe mit 2 bis 14 Kohlenstoffatomen, eine zweiwertige 5- oder 6-gliedrige cycloaliphatische Gruppe mit 5 bis 15 Kohlenstoffatomen oder eine Arylengruppe mit 6 bis 14 Kohlenstoffatomen ist, mit der Maßgabe, daß, wenn Y



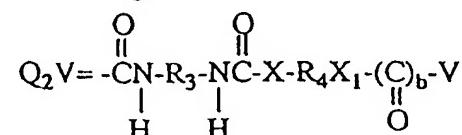
ist, a den Wert 1 hat;

Q ausgewählt ist aus (gezeigt in Bindung an V):

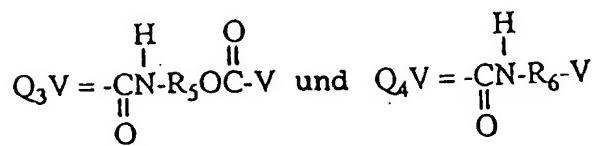
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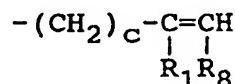


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worin R_4 ein Alkylen mit 2 bis 4 Kohlenstoffatomen ist,
 R_5 ein Alkylen mit 2 bis 10 Kohlenstoffatomen ist,
10 R_6 ein Arylen oder ein Alkyl-substituiertes Arylen mit 6 bis 20 Kohlenstoffatomen ist,
 X -O- oder -NR₇- bedeutet, worin R_7 ein Alkyl mit 1 bis 5 Kohlenstoffatomen ist,
 X_1 -O-, -NH- oder -NR₇- bedeutet,
b den Wert 0 oder 1 besitzt,
V

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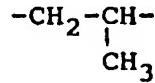
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bedeutet,
c den Wert 0 oder 1 besitzt,
 V_1 die gleiche Bedeutung wie V besitzt, oder für H oder R_9 steht, wenn t den Wert 0 hat,
 R_8 für H oder -COOH steht, mit der Maßgabe, daß, wenn R_8 -COOH ist, R_1 H, c 0 und Q Q₁ bedeutet,
25 R_9 ein Alkyl mit 1 bis 18 Kohlenstoffatomen ist; mit der weiteren Maßgabe, daß, wenn Q Q₂ ist, a für 0
steht;
wenn Q Q₂, Q₃ oder Q₄ ist, R_8 für H steht;
wenn c 1 bedeutet, b 0 ist, Q Q₂ ist und R_1 und R_8 H bedeuten; und
wenn V_1 R₉ ist, m den Wert 0 hat.

30

3. Verfahren nach Anspruch 2, worin der Polyether PE ein Poly(ethylenoxid) (PEO) mit einem Molekulargewicht von 500 bis 10.000, ein Poly(propylenoxid) (PPO) mit einem Molekulargewicht von 500 bis 10.000, ein Poly(ethylenoxidcopropylenoxid) mit einer Zufalls- oder Blockcopolymerstruktur in den Verhältnissen von PEO:PPO von 1:30 bis 30:1 mit einem Molekulargewicht von 500 bis 10.000 oder ein Poly(tetramethylenoxid) mit einem Molekulargewicht von 500 bis 10.000 ist.
4. Verfahren nach Anspruch 3, worin der Polyether PE ein Poly(ethylenoxid) mit einem Molekulargewicht von 1000 bis 8000 oder ein Poly(ethylenoxidcopropylenoxid) mit einem Molekulargewicht von 1000 bis 10.000 ist, und worin a den Wert 1 und R_2

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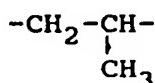


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bedeutet.

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5. Verfahren nach Anspruch 3, worin der Polyether ein Poly-(propylenoxid) mit einem Molekulargewicht von 1000 bis 8000 ist, a den Wert 1 hat und R_2 für



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steht.

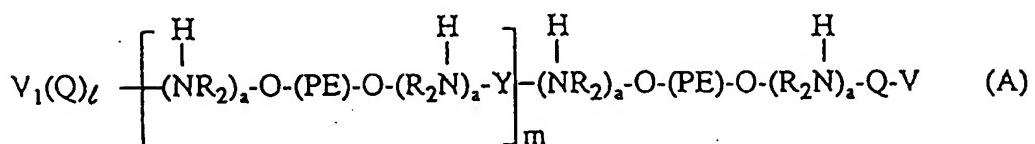
6. Verfahren nach Anspruch 3, worin QV $Q_2 V$ ist, worin in $Q_2 R_3$ ein zweiwertiger Rest ist, erhalten durch Entfernen der zwei NCO-Gruppen aus einem Diisocyanat, ausgewählt aus der Gruppe bestehend aus Ethylen-diisocyanat, 1,2-Diisocyanatopropan, 1,3-Diisocyanatopropan, 1,6-Diisocyanatohexan, 1,2-Diisocyanatocyclohexan, 1,3-Diisocyanatocyclohexan, 1,4-Diisocyanatobenzol, Bis-(4-isocyanatocyclohexyl)-methan, Bis-(4-isocyanatocyclohexenyl)methan, Bis-(4-isocyanatophenyl)methan, 2,6- und 2,4-Toluoldiisocyanat; 3,3'-Dichlor-4,4'-diisocyanatobiphenyl; 1,5-Diisocyanatonaphthalin, hydrierter Toluoldiisocyanat; 1-Isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexan (= Isophorondiisocyanat); 2,2,4-(2,4,4)-Trimethylhexan-1,6-diisocyanat, 2,2'-Diisocyanatodiethylfumarat; 1,5-Diisocyanato-1-carboxypentan; 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- und 2,3-Diisocyanatonaphthalin; 2,4- und 2,7-Diisocyanato-1-methylnaphthalin; 4,4'-Diisocyanatobiphenyl; 4,4'-Diisocyanato-3,3'-diisocyanato-6(7)-methylnaphthalin; 4,4'-Diisocyanato-2,2'-dimethylbiphenyl; Bis-(4-isocyanatophenyl)ethan; und Bis-(4-isocyanatophenyl)-ether, und $V-(CO)_5-X_1-R_4-X$ -der Rest, erhalten durch Entfernen des aktiven Wasserstoffatoms aus einer Hydroxyl- oder Aminogruppe einer Verbindung, ausgewählt aus der Gruppe, bestehend aus 2-Hydroxyethylacrylat und -methacrylat, 2- und 3-Hydroxypropylacrylat und -methacrylat; 4-Hydroxybutylacrylat und -methacrylat; Glycerindimethacrylat; Hydroxyethylmaleat und -fumarat; 2-Hydroxyethyl- und 4-hydroxybutylvinylether; N-tert.-Butylaminoethylmethacrylat, N-(3-Hydroxypropyl)methacrylamid; Vinylbenzylalkohol; und Allylalkohol, ist.
7. Verfahren nach Anspruch 6, worin das Diisocyanat Isophorondiisocyanat, 2,2,4-(2,4,4)-Trimethylhexan-1,6-diisocyanat, 2,4-Toluoldiisocyanat oder 2,6-Toluoldiisocyanat ist, und die den aktiven Wasserstoff enthaltende Vinylverbindung 2-Hydroxyethylmethacrylat, 2-Hydroxyethylacrylat oder N-tert.-Butylaminoethylmethacrylat ist.
8. Verfahren nach Anspruch 3, worin QV $Q_3 V$ ist, und $V-COO-R_5-$ der Rest, erhalten durch Entfernen der NCO-Gruppe von einer Isocyanatverbindung, ausgewählt aus der Gruppe, bestehend aus 2-Isocyanatoethylmethacrylat, 2-Isocyanatoethylacrylat, 3-Isocyanatopropylmethacrylat, 1-Methyl-2-isocyanatoethylmethacrylat, und 1,1-Dimethyl-2-isocyanatoethylacrylat ist.
9. Verfahren nach Anspruch 8, worin die Isocyanatverbindung 2-Isocyanatoethylmethacrylat ist.
10. Verfahren nach Anspruch 3, worin QV $Q_4 V$ ist, und $V-R_6-$ der Rest, erhalten durch Entfernen der NCO-Gruppe aus 2-Isocyanatobutylvinylether, Styrolisocyanat oder m-Isopropenyl- α,α -dimethylbenzylisocyanat, ist.
11. Verfahren nach Anspruch 10, worin das Isocyanat m-Isopropenyl- α,α -dimethylbenzylisocyanat ist.
12. Verfahren nach Anspruch 4, worin QV $Q_3 V$ ist, und $V-COO-R_5-$ der Rest, erhalten durch Entfernen der NCO-Gruppe von einer Isocyanatverbindung, ausgewählt aus der Gruppe, bestehend aus 2-Isocyanatoethylmethacrylat, 2-Isocyanatoethylacrylat, 3-Isocyanatopropylmethacrylat, 1-Methyl-2-isocyanatoethylmethacrylat, und 1,1-Dimethyl-2-isocyanatoethylacrylat, ist.
13. Verfahren nach Anspruch 4, worin QV $Q_4 V$ ist, und $V-R_6-$ der Rest, erhalten durch Entfernen der NCO-Gruppe von 2-Isocyanatobutylvinylether, Styrolisocyanat, oder m-Isopropenyl- α,α -dimethylbenzylisocyanat, ist.
14. Verfahren nach Anspruch 5, worin QV $Q_3 V$ ist, und $V-COO-R_5-$ der Rest, erhalten durch Entfernen der NCO-Gruppe von einer Isocyanatverbindung, ausgewählt aus der Gruppe, bestehend aus 2-Isocyanatoethylmethacrylat, 2-Isocyanatoethylacrylat, 3-Isocyanatopropylmethacrylat, 1-Methyl-2-isocyanatoethylmethacrylat und 1,1-Dimethyl-2-isocyanatoethylacrylat, ist.
15. Verfahren nach Anspruch 5, worin QV $Q_4 V$ ist, und $V-R_6-$ der Rest, erhalten durch Entfernen der NCO-Gruppe aus 2-Isocyanatobutylvinylether, Styrolisocyanat oder m-Isopropenyl- α,α -dimethylbenzylisocyanat ist.
16. Verfahren nach Anspruch 12, worin die Isocyanatverbindung 2-Isocyanatoethylmethacrylat ist.
17. Verfahren nach Anspruch 13, worin das Isocyanat m-Isopropenyl- α,α -dimethylbenzylisocyanat ist.

18. Verfahren nach Anspruch 14, worin das Isocyanat 2-Isocyanatoethylmethacrylat ist.
19. Verfahren nach Anspruch 15, worin das Isocyanat m-Isopropenyl- α,α -dimethylbenzylisocyanat ist.
- 5 20. Verfahren nach Anspruch 2, worin das PE Poly(ethylenoxid), Poly(propylenoxid) oder Poly(ethylen-copolyoxido) ist, und QV Q₂V, Q₃V oder Q₄V ist.
21. Verfahren nach Anspruch 20, worin QV Q₃V oder Q₄V bedeutet, und a den Wert 1 hat.
- 10 22. Verfahren nach Anspruch 1, worin (B-1) ein Fluor-enthaltendes Monomeres ist, das mindestens 3 Fluoratome enthält, ausgewählt aus der Gruppe, bestehend aus Hexafluorisopropylacrylat und -methacrylat, Perfluorcyclohexylacrylat und -methacrylat, Pentafluorstyrol und den Acrylat- oder Methacrylate-stern oder Amiden der Formel
- 15
- 20
- $$\begin{array}{c} \text{CH}_2=\text{C}-\text{COX}(\text{CH}_2)_r-\text{W}-\text{R}_f \\ | \\ \text{R}_1 \end{array} \quad (\text{I})$$
- worin
- R_f -(CF₂)_tCF₂L oder -(CF₂CF₂)_qOCF(CF₃)₂ bedeutet,
- R₁ für ein Wasserstoffatom oder eine Methylgruppe steht,
- X für ein Sauerstoffatom oder -NR₇- steht, worin R₇ eine Alkylgruppe mit 1-5 Kohlenstoffatomen bedeutet,
- r eine ganze Zahl von 1-4 ist,
- t eine ganze Zahl von 0-14 ist,
- q eine ganze Zahl von 1-3 ist;
- L für ein Wasserstoff- oder ein Fluoratom steht, mit der Maßgabe, daß, wenn t den Wert 0 hat, L für ein Fluoratom steht; und W eine direkte Bindung oder eine zweiwertige Gruppe der Struktur -NR₇-CO-; -NR₇SO₂-(CH₂)_r; -NR₇SO₂-; -S-(CH₂)_r; -NR₇-(CH₂)_r-NR₇SO₂-; oder -NHCO- ist.
- 25
- 30
- 35
23. Verfahren nach Anspruch 1, worin (B-1) ein fluoriertes Monomeres, ausgewählt aus der Gruppe, bestehend aus Hexafluorisopropylacrylat, Hexafluorisopropylmethacrylat oder eine Verbindung der Struktur (I), wie in Anspruch 22 definiert, worin W eine direkte Bindung und L ein Fluoratom ist, ist.
24. Verfahren nach Anspruch 22, worin X ein Sauerstoffatom ist, W eine direkte Bindung ist, R₁ ein Wasserstoffatom ist, r den Wert 2 besitzt, t den Wert 6 bis 10 besitzt, und L ein Fluoratom ist; oder worin r den Wert 1 oder 2 besitzt, t den Wert 1 bis 4 besitzt und L ein Fluoratom ist, oder worin R₁ eine Methylgruppe bedeutet, r den Wert 2 besitzt, t den Wert 4 bis 10 besitzt und L ein Fluoratom ist.
- 40
25. Verfahren nach Anspruch 22, worin r den Wert 1 oder 2 besitzt, t den Wert 1 bis 4 besitzt und L ein Fluoratom ist.
- 45
26. Verfahren nach Anspruch 22, worin R für eine Methylgruppe steht, r den Wert 2 besitzt und t den Wert 4 bis 10 besitzt und L ein Fluoratom bedeutet.
27. Verfahren nach Anspruch 1, worin (B-2) ein Silicon-enthaltendes Vinylmonomeres ist, das ein Oligoisoxanylsilylalkylacrylat oder -methacrylat mit 2 bis 10 Siliciumatomen ist.
- 50
28. Verfahren nach Anspruch 27, worin das Monomere aus der Gruppe, bestehend aus Tris(trimethylsiloxy)silylpropyl(meth)acrylat, Triphenyldimethyldisiloxanyl(meth)acrylat, Pentamethyl-disiloxanyl(meth)acrylat, tert.-Butyltetramethyldisiloxylethyl(meth)acrylat, Methyldi(trimethylsiloxy)-silylpropylglyceryl(meth)acrylat; Pentamethyldisiloxanyl(meth)acrylat; Heptamethylcyclotetrasilox-ymethylmethacrylat; Heptamethylcyclotetrasiloxylpropylmethacrylat; (Trimethylsilyl)-decamethylpentasiloxypropylmethacrylat; und Undecamethylpentasiloxypropylmethacrylat, ist.
- 55
29. Verfahren nach Anspruch 28, worin das Monomere Tris(trimethylsiloxy)silylpropylmethacrylat ist.

30. Verfahren nach Anspruch 1, worin die Komponente (B) 40 bis 80 Gew.-% des Copolymeren ausmacht.
31. Verfahren nach Anspruch 30, worin die Komponente (B) 50 bis 70 Gew.-% des Copolymeren ausmacht.
- 5 32. Verfahren nach Anspruch 1, worin die Komponente (C) ein Monomeres, ausgewählt aus der Gruppe, bestehend aus Methylacrylat, Ethylacrylat, n- und Isopropylacrylat, Cyclohexylacrylat, Trimethylcyclohexylacrylat, Phenylacrylat, Benzylacrylat und den entsprechenden Methacrylaten; Furfurylacrylat und -methacrylat; Methoxyethyl-, Ethoxyethyl- und Ethoxyethoxyethylacrylat und -methacrylat; 2-Hydroxyethylacrylat und -methacrylat; 3-Hydroxypropylacrylat, -methacrylat und -methacrylamid; Glycidylmethacrylat; N,N-Dimethylacrylamid; N-Isopropylacrylamid; N-Vinylacetamid; N-Vinylpyrrolidon; Dimethylaminoethylmethacrylat und -methacrylamid; Acryl- und Methacrylsäure, Vinylsulfonsäure, Styrol, 4-Styrolsulfonsäure und 2-Methacrylamido-2-methylpropan sulfonsäure und ihren Salzen und Gemischen davon, ist.
- 10 33. Verfahren nach Anspruch 32, worin das Monomere Methoxyethylacrylat und Methoxyethylmethacrylat, Ethoxyethylacrylat und Ethoxyethylmethacrylat; Methylmethacrylat; Methylacrylat, 2-Hydroxyethylmethacrylat; N-Vinylpyrrolidon; N,N-Dimethylacrylamid und Styrol, und Ethoxyethoxyethylacrylat oder Gemische davon ist.
- 15 34. Verfahren nach Anspruch 1, worin die Komponente (C) 5 bis 60 Gew.-% des Copolymeren ausmacht.
- 20 35. Verfahren nach Anspruch 34, worin die Komponente (C) 10 bis 50 Gew.-% des Copolymeren ausmacht.
- 25 36. Verfahren nach Anspruch 1, zur Herstellung einer Kontaktlinse.
- 30 37. Verfahren nach Anspruch 1, worin der Polyether PE ein fluorierter Polyether mit einem Molekulargewicht von 600 bis 5000 der Struktur HO-CH₂CF₂(C₂F₄O)_x(CF₂O)_y-CF₂CH₂-OH, worin x und y unabhängig voneinander ganze Zahlen von 6 bis 50 sind, ist.
38. Verfahren nach Anspruch 4, worin die Menge der Komponente (C) 0 beträgt.
39. Verfahren nach Anspruch 4, worin die Komponente (A) 15 bis 30 Gew.-% des Copolymeren beträgt.
- 40 40. Verfahren nach Anspruch 5, worin die Komponente (A) 30 bis 60 Gew.-% des Copolymeren beträgt.
41. Verfahren nach Anspruch 38 zur Herstellung einer Kontaktlinse.
42. Verwendung eines Copolymeren nach Anspruch 1 zur Herstellung einer Kontaktlinse.
- 40 43. Kontaktlinse, umfassend ein Copolymeres nach Anspruch 1.
44. Kontaktlinse, bestehend im wesentlichen aus einem Copolymeren nach Anspruch 1.
- 45 **Revendications**
Revendications pour les Etats contractants suivants : AT, BE, CH, LI, DE, DK, FR, GB, GR, IT, LU, NL, SE
- 50 1. Copolymère qui est perméable à l'oxygène, souple, mouillable, biocompatible et convenant à une utilisation dans des dispositifs ophthalmiques, tels que des lentilles de contact, ce copolymère comprenant le produit de polymérisation de
 - (A) 10 à 80 % en poids d'un polyéther téléchérique vinylique, ou un mélange de celui-ci,
 - (B) 90 à 20 % en poids de
 - (B-1) un monomère éthyléniquement insaturé fluoré, ou
 - (B-2) un monomère éthyléniquement insaturé contenant du silicium, ou un mélange de monomère (B-1) et de monomère (B-2), et
 - (C) 0 à 60 % en poids d'un monomère éthyléniquement insaturé ou d'un mélange de monomères autres que le monomère (B-1) ou le monomère (B-2).

2. Copolymère selon la revendication 1, dans lequel le polyéther téléchérique de vinyle (A) a la formule (A) :

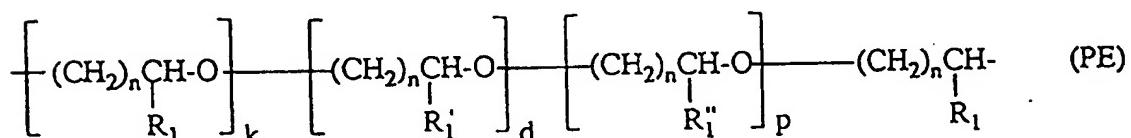
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dans laquelle PE a un poids moléculaire moyen (PM) d'environ 500 à environ 10 000 et a la formule :

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dans laquelle n est compris entre 1 et 3,

k, d et p sont des nombres entiers de 0 à 300, et la somme k + d + p est comprise entre 7 et 300,

R₁, R₁' et R₁'' sont indépendamment les uns des autres des hydrogène ou des méthyles, à la condition que si n est égal à 3, R₁,

R₁' et R₁'' sont des hydrogène,

a est zéro ou 1,

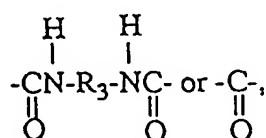
m est un nombre entier de zéro à 2,

l est zéro ou 1

30 R₂ est un alkylène linéaire ou ramifié avec 2 à 4 atomes de carbone ;

Y est

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dans lequel R₃ est un groupe aliphatique divalent avec 2 à 14 atomes de carbone, un groupe cycloaliphatique divalent à 5 ou 6 membres avec 5 à 15 atomes de C, ou un groupe arylène avec 6 à 14 atomes de C, à la condition que si Y est

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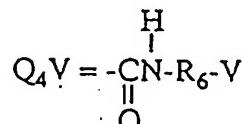
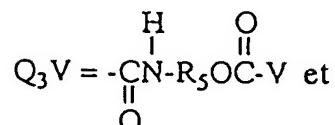
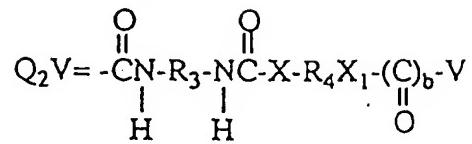
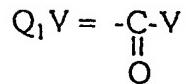


a est égal à 1 ;

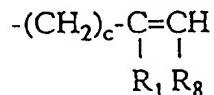
Q est choisi parmi (présenté attaché à V)

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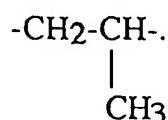
dans lesquels R_4 est un alkylène de 2 à 4 atomes de carbone,
 R_5 est un alkylène de 2 à 10 atomes de carbone,
 R_6 est un arylène ou un arylène de 6 à 20 atomes de carbone substitué par des alkyles,
 X est $-O-$ ou $-NR_7-$, dans lequel R_7 est un alkyle de 1 à 5 atomes de carbone,
 X_1 est $-O-$, $-NH-$ ou $-NR_7-$,
 b est égal à zéro ou 1
 V est



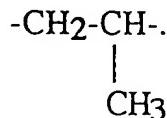
c est égal à zéro ou 1

35 V_1 a la même signification que V , ou est H ou R_9 , quand I est égal à zéro,
 R_8 est H ou $-COOH$, à la condition que, si R_8 est $-COOH$, R_1 est H , c est égal à zéro, et Q est Q_1 ;
 R_9 est un alkyle de 1 à 18 atomes de carbone ;
avec la condition supplémentaire que
quand Q est Q_2 , a est égal à zéro ;
40 quand Q est Q_2 , Q_3 ou Q_4 , R_8 est H ;
quand c est égal à 1, b est égal à 0, Q est Q_2 et R_1 et R_8 sont H ; et
quand V_1 est R_9 , m est égal à zéro.

- 45 3. Copolymère selon la revendication 2, dans lequel le polyéther PE est un poly(oxyde d'éthylène) (PEO)
de PM 500 à 10 000, un poly(oxyde propylène) (PPO) de PM 500 à 10 000, un poly(oxyde d'éthylène-co-oxyde de propylène) de structure copolymère au hasard ou bloc dans les rapports de PEO:PPO de 1:30 à 30:1 et de PM 500 à 10 000 ou un poly(oxyde de tétraméthylène) de PM 500 à 10 000.
- 50 4. Copolymère selon la revendication 3, dans lequel le polyéther PE est un poly(oxyde d'éthylène) de PM 1000 à 8000, ou un poly(oxyde d'éthylène-co-oxyde de propylène) de PM 1000 à 10 000 et dans lequel a est égal à 1 et R_2 est



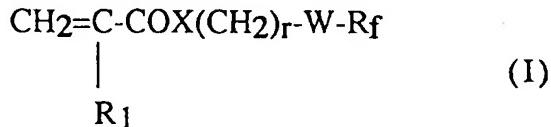
5. Un copolymère selon la revendication 3, dans lequel le polyéther est un poly(oxyde de propylène) de PM 1000 à 8000, a est égal à 1 et R₂ est



- 10
6. Copolymère selon la revendication 3, dans lequel QV est QV₂, dans lequel Q₂R₃ est un radical divalent obtenu en éliminant les deux groupes -NCO d'un diisocyanate choisi dans le groupe constitué de diisocyanate d'éthylène, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatobenzène, bis(4-isocyanato-cyclohexyl)méthane, bis(4-isocyanatocyclohexényl)méthane, bis(4-isocyanatophényl)méthane, diisocyanate de 2,6- et 2,4-toluène, 3,3'-dichloro-4,4'-diisocyanatobiphényle ; 1,5-diisocyanatonaphthalène, diisocyanate de toluène hydrogéné ; 1-isocyanatométhyl-5-isocyanato-1,3,3-triméthylcyclohexane (= diisocyanate d'isophorone) ; 2,2,4-(2,4,4)-triméthylhexane-1,6-diisocyanate, fumarate de 2,2'-diisocyanatodiéthyle ; 1,5-diisocyanato-1-carboxypentane ; 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- et 2,3-diisocyanatonaphthalène ; 2,4- et 2,7-diisocyanato-1-méthynaphthalène ; 4,4'-diisocyanatobiphényle ; 4,4'-diisocyanato-3,3'-diisocyanato-6(7)-méthynaphthalène ; 4,4'-diisocyanato-2,2'-diméthylbiphényle ; bis(4-isocyanatophényl)-éthane ; et bis(4-isocyanatophényl)éther, et V-(CO)_b-X₁-R₄-X- est le radical obtenu en éliminant l'atome d'hydrogène actif d'un groupe hydroxyle ou amino d'un composé choisi dans le groupe constitué d'acrylate et méthacrylate de 2-hydroxyéthyle, acrylate et méthacrylate de 2- et 3-hydroxypropyle ; acrylate et méthacrylate de 4-hydroxybutyle; diméthacrylate de glycérol ; maléate et fumarate d'hydroxyéthyle, éther vinylique de 2-hydroxyéthyle et 4-hydroxybutyle ; méthacrylate de N-tert.butylaminoéthyle, N-(3-hydroxypropyl)-méthacrylamide ; alcool vinylbenzylique ; et alcool allylique.
- 20
7. Copolymère selon la revendication 6, dans lequel le diisocyanate est le diisocyanate d'isophorone, le 2,24-(2,4,4)-triméthylhexane-1,6-diisocyanate, le diisocyanate de 2,4-toluène ou le diisocyanate de 2,6-toluène, et le composé vinylique contenant l'hydrogène actif est le méthacrylate de 2-hydroxyéthyle, l'acrylate de 2-hydroxyéthyle ou le méthacrylate de N-tert.butylaminoéthyle.
- 30
8. Copolymère selon la revendication 3, dans lequel QV est Q₃V et V-COO-R₅- est le radical obtenu en éliminant le groupe -NCO d'un composé isocyanate choisi parmi le groupe constitué de méthacrylate de 2-isocyanatoéthyle, acrylate de 2-isocyanatoéthyle, méthacrylate de 3-isocyanatopropyle, méthacrylate de 1-méthyl-2-isocyanatoéthyle, et acrylate de 1,1-diméthyl-2-isocyanatoéthyle.
- 35
9. Copolymère selon la revendication 8, dans lequel le composé isocyanate est le méthacrylate de 2-isocyanatoéthyle.
- 40
10. Copolymère selon la revendication 3, dans lequel QV est Q₄V et V-R₆- est le radical obtenu en éliminant le groupe -NCO d'un éther vinylique de 2-isocyanatobutyle, d'un isocyanate de styrène, ou d'un isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
- 45
11. Copolymère selon la revendication 10, dans lequel l'isocyanate est l'isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
- 50
12. Copolymère selon la revendication 4, dans lequel QV est Q₃V et V-COO-R₅- est le radical obtenu en éliminant le groupe -NCO d'un composé isocyanate choisi parmi le groupe constitué de méthacrylate de 2-isocyanatoéthyle, acrylate de 2-isocyanatoéthyle, méthacrylate de 3-isocyanatopropyle, méthacrylate de 1-méthyl-2-isocyanatoéthyle, et acrylate de 1,1-diméthyl-2-isocyanatoéthyle.
- 55
13. Copolymère selon la revendication 4, dans lequel QV est Q₄V et V-R₆- est le radical obtenu en éliminant le groupe -NCO d'un éther vinylique de 2-isocyanatobutyle, d'un isocyanate de styrène, ou d'un isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.

14. Copolymère selon la revendication 5, dans lequel QV est Q_3V et $V-COO-R_5-$ est le radical obtenu en éliminant le groupe -NCO d'un composé isocyanate choisi parmi le groupe constitué de méthacrylate de 2-isocyanatoéthyle, acrylate de 2-isocyanatoéthyle, méthacrylate de 3-isocyanatopropyle, méthacrylate de 1-méthyl-2-isocyanatoéthyle, et acrylate de 1,1-diméthyl-2-isocyanatoéthyle.
- 5 15. Copolymère selon la revendication 5, dans lequel QV est Q_4V et $V-R_6-$ est le radical obtenu en éliminant le groupe -NCO d'un éther vinylique de 2-isocyanatobutyle, d'un isocyanate de styrène, ou d'un isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
- 10 16. Copolymère selon la revendication 12, dans lequel le composé isocyanate est le méthacrylate de 2-isocyanatoéthyle.
17. Copolymère selon la revendication 13, dans lequel l'isocyanate est l'isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
- 15 18. Copolymère selon la revendication 14, dans lequel le composé isocyanate est le méthacrylate de 2-isocyanatoéthyle.
19. Copolymère selon la revendication 15, dans lequel l'isocyanate est l'isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
- 20 20. Copolymère selon la revendication 2, dans lequel PE est du poly(oxyde d'éthylène), poly(oxyde de propylène) ou poly(oxyde d'éthylène-co-oxyde de propylène) et QV est Q_2V , Q_3V ou Q_4V .
- 25 21. Copolymère selon la revendication 20, dans lequel QV est Q_3V ou Q_4V et a est égal à 1.

22. Copolymère selon la revendication 1, dans lequel (B-1) est un monomère contenant du fluor contenant au moins trois atomes de fluor, choisi dans le groupe constitué de d'acrylate et de méthacrylate d'hexafluoroisopropyle, d'acrylate et de méthacrylate de perfluorocyclohexyle, de pentafluorostyrène et des esters ou amides d'acrylate ou de méthacrylate de formule



- 35 dans laquelle
 R_f est $-(\text{CF}_2)_l\text{CF}_2\text{L}$ ou $-(\text{CF}_2\text{CF}_2)_q\text{OCF}(\text{CF}_3)_2$,
 R_1 est un hydrogène ou un méthyle,
 X est un oxygène ou $-\text{NR}_7-$ dans lequel R_7 est un groupe alkyle avec 1 à 5 atomes de carbone,
 r est un nombre entier de 1 à 4,
 t est un nombre entier de 0 à 14,
 q est un nombre entier de 1 à 3 ;
 40 L est un hydrogène ou un fluor, à la condition que, quand t est égal à 0, L est un fluor ; et
 W est une liaison directe ou un groupe divalent de structure $-\text{NR}_7-\text{CO}-$; $-\text{NR}_7\text{SO}_2-(\text{CH}_2)_r-$; $-\text{NR}_7\text{SO}_2-$;
 $-S-(\text{CH}_2)_r-$; $-\text{NR}_7-(\text{CH}_2)_r-\text{NR}_7\text{SO}_2-$; ou $-\text{NHCO}-$.

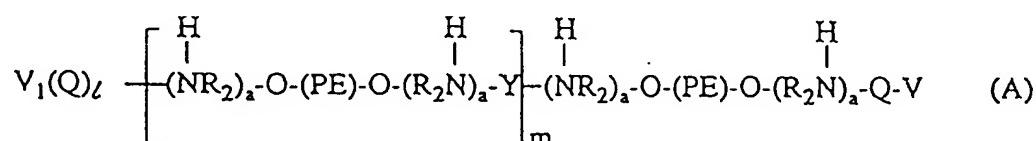
- 45 23. Copolymère selon la revendication 1, dans lequel (B-1) est un monomère fluoré choisi dans le groupe constitué d'acrylate d'hexafluoroisopropyle, de méthacrylate d'hexafluoroisopropyle ou un composé de structure (I), comme défini dans la revendication 22, dans lequel W est une liaison directe et L est un fluor.
- 50 24. Copolymère selon la revendication 22, dans lequel X est un oxygène, W est une liaison directe, R_1 est un hydrogène, r est égal à 2, t est compris entre 6 et 10 et L est un fluor ; ou dans lequel r est égal à 1 ou 2, t est compris entre 1 et 4 et L est un fluor, ou dans lesquels R_1 est un méthyle, r est égal à 2, t est compris entre 4 et 10 et L est un fluor.

25. Copolymère selon la revendication 22, dans lequel r est égal à 1 ou 2, t est compris entre 1 et 4 et L est un fluor.
26. Copolymère selon la revendication 22, dans lequel R est un méthyle, r est égal à 2, et t est compris entre 4 et 10 et L est un fluor.
27. Copolymère selon la revendication 1, dans lequel (B-2) est un monomère vinylique contenant du silicium qui est un acrylate ou un méthacrylate d'oligosiloxanyl-silyl-alkyle contenant de 2 à 10 atomes de silicium.
28. Copolymère selon la revendication 27, dans lequel le monomère est choisi dans le groupe constitué de (méth)acrylate de tris(triméthylsiloxy)-silylpropyle, (méth)acrylate de triphényldiméthyl-disiloxanyl-méthyle, acrylate de pentaméthyl-disiloxanyl-méthyle, (méth)acrylate de tert-butyltétraméthyl-disiloxanyl-méthyle, (méth)acrylate de méthyl-di(triméthylsiloxy)silylpropyle-glycéryle ; méthacrylate de pentaméthyl-di-siloxanyl-méthyle, méthacrylate d'heptaméthylcyclotétra-siloxyméthyle, méthacrylate d'heptaméthylcyclotérasiloxo-propyle ; méthacrylate de (triméthylsilyl)decaméthyl-pentasiloxy-propyle ; et méthacrylate de undécaméthylpentasiloxypropyle.
29. Copolymère selon la revendication 28, dans lequel le monomère est le méthacrylate de tris-(triméthylsiloxy)-silyl-propyle.
30. Copolymère selon la revendication 1, dans lequel le composant (B) constitue 40 à 80 % en poids dudit copolymère.
31. Copolymère selon la revendication 30, dans lequel le composant (B) constitue 50 à 70 % en poids dudit copolymère.
32. Copolymère selon la revendication 1, dans lequel le composant (C) est choisi dans le groupe constitué d'acrylate de méthyle, acrylate d'éthyle, acrylate de n- et isopropyle, acrylate de cyclohexyle, acrylate de triméthyl-cyclohexyle, acrylate de phényle, acrylate de benzyle et les méthacrylates correspondants ; acrylate et méthacrylate de furfuryle ; acrylate et méthacrylate de méthoxy-éthyl-, d'éthoxy-éthyl-, et d'éthoxy-éthoxy-éthyle ; acrylate et méthacrylate de 2-hydroxyéthyle ; acrylate, méthacrylate et méthylacrylamide de 3-hydroxypropyle ; méthacrylate de glycidyle ; N,N-diméthylacrylamide ; N-isopropyl-acrylamide ; N-vinylacétamide ; N-vinyl-pyrrolidone ; méthacrylate et méthylacrylamide de diméthylamino-éthyle ; acide acrylique et méthacrylique, acide vinylsulfonique, styrène, acide 4-styrene-sulfonique et acide 2-méthacrylamido-2-méthyl-propane-sulfonique et leurs sels, et de mélanges de ceux-ci.
33. Copolymère selon la revendication 32, dans lequel le monomère est l'acrylate de méthoxy-éthyle et le méthacrylate de méthoxyéthyle, l'acrylate d'éthoxy-éthyle et le méthacrylate d'éthoxy-éthyle ; le méthacrylate de méthyle ; l'acrylate de méthyle, le méthacrylate de 2-hydroxyéthyle ; la N-vinylpyrrolidone ; le N,N-diméthylacrylamide et le styrène et l'acrylate d'éthoxy-éthoxy-éthyle ou des mélanges de ceux-ci.
34. Copolymère selon la revendication 1, dans lequel le composant (C) est compris entre 5 et 60 % en poids dudit copolymère.
35. Copolymère selon la revendication 34, dans lequel le composant (C) est compris entre 10 et 50 % en poids dudit copolymère.
36. Copolymère selon la revendication 1, qui a la forme d'une lentille de contact.
37. Copolymère selon la revendication 1, dans lequel le polyéther PE est un polyéther fluoré de PM 600 à 5000 de structure HO-CH₂CF₂(C₂F₄O)_x(CF₂O)_yCF₂CH₂-OH, dans lequel x et y sont indépendamment l'un de l'autre des nombres entiers de 6 à 50.
38. Copolymère selon la revendication 4, dans lequel la quantité de composant (C) est égale à zéro.

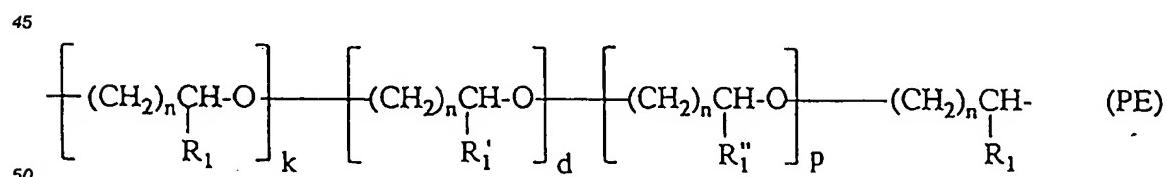
39. Copolymère selon la revendication 4, dans lequel le composant (A) est compris entre 15 et 30 % en poids dudit copolymère.
40. Copolymère selon la revendication 5, dans lequel le composant (A) est compris entre 30 et 60 % en poids dudit copolymère.
- 5 41. Copolymère selon la revendication 38, qui a la forme d'une lentille de contact.
42. Procédé pour la fabrication d'un copolymère selon la revendication 1, caractérisé par la copolymérisation conventionnelle du mélange de monomères en employant des initiateurs qui génèrent des radicaux libres après application d'une énergie d'activation.
- 10 43. Utilisation d'un copolymère selon la revendication 1 pour la fabrication de lentilles de contact.
- 15 44. Lentille de contact constituée d'un copolymère tel que défini dans la revendication 1.
45. Lentille de contact constituée essentiellement d'un copolymère tel que défini dans la revendication 1.

Revendications pour l'Etat contractant suivant : ES

- 20 1. Procédé pour la fabrication d'un copolymère qui est perméable à l'oxygène, souple, mouillable, biocompatible et convient à une utilisation dans des dispositifs ophthalmiques, tels que des lentilles de contact, ce copolymère comprenant le produit de polymérisation de
- (A) 10 à 80 % en poids d'un polyéther tépéchélique vinylique, ou un mélange de celui-ci,
- 25 (B) 90 à 20 % en poids de
- (B-1) un monomère éthyléniquement insaturé fluoré, ou
- (B-2) un monomère éthyléniquement insaturé contenant du silicone, ou un mélange de monomère (B-1) et de monomère (B-2), et
- (C) 0 à 60 % en poids d'un monomère éthyléniquement insaturé ou d'un mélange de monomères autres que le monomère (B-1) ou le monomère (B-2),
- 30 caractérisé par la copolymérisation conventionnelle du mélange de monomères en employant des initiateurs qui génèrent des radicaux libres après application d'une énergie d'activation.
2. Procédé selon la revendication 1, dans lequel le polyéther tépéchélique vinylique (A) a la formule (A) :



dans laquelle PE a un poids moléculaire moyen (PM) d'environ 500 à environ 10 000 et a la formule :



dans laquelle n est compris entre 1 et 3,

k, d et p sont des nombres entiers de 0 à 300, et la somme k + d + p est comprise entre 7 et 300,

55 R₁, R_{1'} et R_{1''} sont indépendamment les uns des autres des hydrogène ou des méthyles, à la condition que si n est égal à 3, R₁, R_{1'} et R_{1''} sont des hydrogène,

a est zéro ou 1,

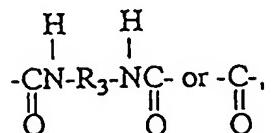
m est un nombre entier de zéro à 2,

I est zéro ou 1

R₂ est un alkylène linéaire ou ramifié avec 2 à 4 atomes de carbone ;

Y est

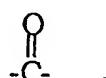
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dans lequel R₃ est un groupe aliphatique divalent avec 2 à 14 atomes de carbone, un groupe cycloaliphatique divalent à 5 ou 6 membres avec 5 à 15 atomes de C, ou un groupe arylène avec 6 à 14 atomes de C, à la condition que si Y est

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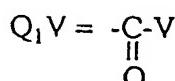


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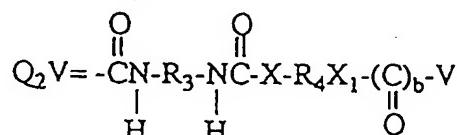
a est égal à 1 ;

Q est choisi parmi (présenté attaché à V)

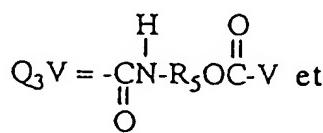
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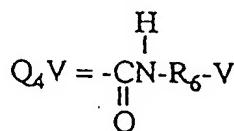
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dans lesquels R₄ est un alkylène de 2 à 4 atomes de carbone,R₅ est un alkylène de 2 à 10 atomes de carbone,

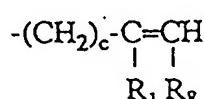
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R₆ est un arylène ou un arylène de 6 à 20 atomes de carbone substitué par des alkyles,X est -O- ou -NR₇- , dans lequel R₇ est un alkyle de 1 à 5 atomes de carbone,X₁ est -O-, -NH- ou -NR₇-,

b est égal à zéro ou 1

V est

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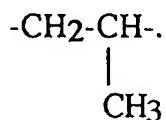
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c est égal à zéro ou 1

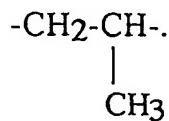
V₁ a la même signification que V, ou est H ou R₉, quand I est égal à zéro,

R_8 est H ou -COOH, à la condition que, si R_8 est -COOH, R_1 est H, c est égal à zéro, et Q est Q_1 ;
 R_9 est un alkyle de 1 à 18 atomes de carbone ;
avec la condition supplémentaire que quand Q est Q_2 , a est égal à zéro ;
quand Q est Q_2 , Q_3 ou Q_4 , R_8 est H ;
5 quand c est égal à 1, b est égal à 0, Q est Q_2 et R_1 et R_8 sont H ; et
quand V_1 est R_9 , m est égal à zéro.

- 10 3. Procédé selon la revendication 2, dans lequel le polyéther PE est un poly(oxyde d'éthylène) (PEO) de PM 500 à 10 000, un poly(oxyde propylène) (PPO) de PM 500 à 10 000, un poly(oxyde d'éthylène-co-oxyde de propylène) de structure copolymère au hasard ou bloc dans les rapports de PEO:PPO de 1:30 à 30:1 et de PM 500 à 10 000 ou un poly(oxyde de tétraméthylène) de PM 500 à 10 000.
- 15 4. Procédé selon la revendication 3, dans lequel le polyéther PE est un poly(oxyde d'éthylène) de PM 1000 à 8000, ou un poly(oxyde d'éthylène-co-oxyde de propylène) de PM 1000 à 10 000 et dans lequel a est égal à 1 et R_2 est



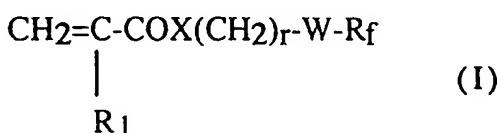
- 25 5. Procédé selon la revendication 3, dans lequel le polyéther est un poly(oxyde de propylène) de PM 1000 à 8000, a est égal à 1 et R_2 est



- 35 6. Procédé selon la revendication 3, dans lequel QV est Q_2V_2 , dans lequel Q_2R_3 est un radical divalent obtenu en éliminant les deux groupes -NCO d'un diisocyanate choisi dans le groupe constitué de diisocyanate d'éthylène, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatobenzène, bis(4-isocyanato-cyclohexyl)méthane, bis(4-isocyanatocyclohexényl)méthane, bis(4-isocyanatophényl)méthane, diisocyanate de 2,6- et 2,4-toluène, 3,3'-dichloro-4,4'-diisocyanatobiphényle ; 1,5-diisocyanatonaphthalène, diisocyanate de toluène hydrogéné ; 1-isocyanatométhyl-5-isocyanato-1,3,3-triméthylcyclohexane (= diisocyanate d'isophorone) ; 2,2,4-(2,4,4)-triméthylhexane-1,6-diisocyanate, fumarate de 2,2'-diisocyanatodiéthyle ; 1,5-diisocyanato-1-carboxypentane ; 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,7- et 2,3-diisocyanatonaphthalène ; 2,4- et 2,7-diisocyanato-1-méthylnaphtalène ; 4,4'-diisocyanatobiphényle ; 4,4'-diisocyanato-3,3'-diisocyanato-6(7)-méthylnaphtalène ; 4,4'-diisocyanato-2,2'-diméthylbiphényle ; bis-(4-isocyanatophényl)-éthane ; et bis(4-isocyanatophényl)éther, et $V\text{-CO}_b\text{-X}_1\text{-R}_4\text{-X}$ - est le radical obtenu en éliminant l'atome d'hydrogène actif d'un groupe hydroxyle ou amino d'un composé choisi dans le groupe constitué d'acrylate et méthacrylate de 2-hydroxyéthyle, acrylate et méthacrylate de 2- et 3-hydroxypropyle ; acrylate et méthacrylate de 4-hydroxybutyle; diméthacrylate de glycérol ; maléate et fumarate d'hydroxyéthyle, éther vinylique de 2-hydroxyéthyle et 4-hydroxy-butyle ; méthacrylate de N-tert.butylaminoéthyle, N-(3-hydroxypropyl)-méthacrylamide ; alcool vinylbenzylique ; et alcool allylique.
- 45 7. Procédé selon la revendication 6, dans lequel le diisocyanate est le diisocyanate d'isophorone, le 2,24-(2,4,4)-triméthylhexane-1,6-diisocyanate, le diisocyanate de 2,4-toluène ou le diisocyanate de 2,6-toluène, et le composé vinylique contenant l'hydrogène actif est le méthacrylate de 2-hydroxyéthyle, l'acrylate de 2-hydroxyéthyle ou le méthacrylate de N-tert.butylaminoéthyle.
- 55 8. Procédé selon la revendication 3, dans lequel QV est Q_3V et $V\text{-COO-R}_5\text{-}$ est le radical obtenu en éliminant le groupe -NCO d'un composé isocyanate choisi parmi le groupe constitué de méthacrylate

de 2-isocyanatoéthyle, acrylate de 2-isocyanatoéthyle, méthacrylate de 3-isocyanatopropyle, méthacrylate de 1-méthyl-2-isocyanatoéthyle, et acrylate de 1,1-diméthyl-2-isocyanatoéthyle.

9. Procédé selon la revendication 8, dans lequel le composé isocyanate est le méthacrylate de 2-isocyanatoéthyle.
10. Procédé selon la revendication 3, dans lequel QV est $Q_4 V$ et $V-R_5-$ est le radical obtenu en éliminant le groupe -NCO d'un éther vinylique de 2-isocyanatobutyle, d'un isocyanate de styrène, ou d'un isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
11. Procédé selon la revendication 10, dans lequel l'isocyanate est l'isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
12. Procédé selon la revendication 4, dans lequel QV est $Q_3 V$ et $V-COO-R_5-$ est le radical obtenu en éliminant le groupe -NCO d'un composé isocyanate choisi parmi le groupe constitué de méthacrylate de 2-isocyanatoéthyle, acrylate de 2-isocyanatoéthyle, méthacrylate de 3-isocyanatopropyle, méthacrylate de 1-méthyl-2-isocyanatoéthyle, et acrylate de 1,1-diméthyl-2-isocyanatoéthyle.
13. Procédé selon la revendication 4, dans lequel QV est $Q_4 V$ et $V-R_5-$ est le radical obtenu en éliminant le groupe -NCO d'un éther vinylique de 2-isocyanatobutyle, d'un isocyanate de styrène, ou d'un isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
14. Procédé selon la revendication 5, dans lequel QV est $Q_3 V$ et $V-COO-R_5-$ est le radical obtenu en éliminant le groupe -NCO d'un composé isocyanate choisi parmi le groupe constitué de méthacrylate de 2-isocyanatoéthyle, acrylate de 2-isocyanatoéthyle, méthacrylate de 3-isocyanatopropyle, méthacrylate de 1-méthyl-2-isocyanatoéthyle, et acrylate de 1,1-diméthyl-2-isocyanatoéthyle.
15. Procédé selon la revendication 5, dans lequel QV est $Q_4 V$ et $V-R_5-$ est le radical obtenu en éliminant le groupe -NCO d'un éther vinylique de 2-isocyanatobutyle, d'un isocyanate de styrène, ou d'un isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
16. Procédé selon la revendication 12, dans lequel le composé isocyanate est le méthacrylate de 2-isocyanatoéthyle.
17. Procédé selon la revendication 13, dans lequel l'isocyanate est l'isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
18. Procédé selon la revendication 14, dans lequel le composé isocyanate est le méthacrylate de 2-isocyanatoéthyle.
19. Procédé selon la revendication 15, dans lequel l'isocyanate est l'isocyanate de m-isopropényl-alpha,alpha-diméthylbenzyle.
20. Procédé selon la revendication 2, dans lequel PE est du poly(oxyde d'éthylène), poly(oxyde de propylène) ou poly(oxyde d'éthylène-co-oxyde de propylène) et QV est $Q_2 V$, $Q_3 V$ ou $Q_4 V$.
21. Procédé selon la revendication 20, dans lequel QV est $Q_2 V$, $Q_3 V$ ou $Q_4 V$ et α est égal à 1.
22. Procédé selon la revendication 1, dans lequel (B-1) est un monomère contenant du fluor contenant au moins trois atomes de fluor, choisi dans le groupe constitué de d'acrylate et de méthacrylate d'hexafluoroisopropyle, d'acrylate et de méthacrylate de perfluorocyclohexyle, de pentafluorostyrène et des esters ou amides d'acrylate ou de méthacrylate de formule



dans laquelle

R₁ est -(CF₂)_tCF₂L ou -(CF₂CF₂)_qOCF(CF₃)₂,

R₁ est un hydrogène ou un méthyle,

X est un oxygène ou -NR₇- dans lequel R₇ est un groupe alkyle avec 1 à 5 atomes de carbone,

5 r est un nombre entier de 1 à 4,

t est un nombre entier de 0 à 14,

q est un nombre entier de 1 à 3 ;

L est un hydrogène ou un fluor, à la condition que, quand t est égal à 0, L est un fluor ; et

10 W est une liaison directe ou un groupe divalent de structure -NR₇-CO- ; -NR₇SO₂-(CH₂)_r- ; -NR₇SO₂- ; -S-(CH₂)_r- ; -NR₇-(CH₂)_r-NR₇SO₂- ; ou -NHCO-.

23. Procédé selon la revendication 1, dans lequel (B-1) est un monomère fluoré choisi dans le groupe constitué d'acrylate d'hexafluoroisopropyle, de méthacrylate d'hexafluoroisopropyle ou un composé de structure (I), comme défini dans la revendication 22, dans lequel W est une liaison directe et L est un fluor.

15 24. Procédé selon la revendication 22, dans lequel X est un oxygène, W est une liaison directe, R₁ est un hydrogène, r est égal à 2, t est compris entre 6 et 10 et L est un fluor ; ou dans lequel r est égal à 1 ou 2, t est compris entre 1 et 4 et L est un fluor, ou dans lesquels R₁ est un méthyle, r est égal à 2, t est compris entre 4 et 10 et L est un fluor.

20 25. Procédé selon la revendication 22, dans lequel r est égal à 1 ou 2, t est compris entre 1 et 4 et L est un fluor.

25 26. Procédé selon la revendication 22, dans lequel R est un méthyle, r est égal à 2 et t est compris entre 4 et 10 et L est un fluor.

30 27. Procédé selon la revendication 1, dans lequel (B-2) est un monomère vinylique contenant du silicium qui est un acrylate ou un méthacrylate d'oligosiloxanyl-silyl-alkyle contenant de 2 à 10 atomes de silicium.

35 28. Procédé selon la revendication 27, dans lequel le monomère est choisi dans le groupe constitué de (méth)acrylate de tris(triméthylsiloxy)-silylpropyle, (méth)acrylate de triphényldiméthyl-disiloxanyl-méthyle, acrylate de pentaméthyl-disiloxanyl-méthyle, (méth)acrylate de tert-butyl-tétraméthyl-disiloxanyl-éthyle, (méth)acrylate de méthyl-di(triméthylsiloxy)silylpropyle-glycéryle ; méthacrylate de pentaméthyl-di-siloxanyl-méthyle, méthacrylate d'heptaméthylcyclotétra-siloxyméthyle ; méthacrylate d'heptaméthylcycloté-trasiloxy-propyle ; méthacrylate de (triméthylsilyl)decaméthyl-pentasiloxy-propyle ; et méthacrylate de undécaméthylpentasiloxypropyle.

40 29. Procédé selon la revendication 28, dans lequel le monomère est le méthacrylate de tris(triméthylsiloxy)-silyl-propyle.

30 30. Procédé selon la revendication 1, dans lequel le composant (B) constitue 40 à 80 % en poids dudit copolymère.

45 31. Procédé selon la revendication 30, dans lequel le composant (B) constitue 50 à 70 % en poids dudit copolymère.

32. Procédé selon la revendication 1, dans lequel le composant (C) est choisi dans le groupe constitué 50 d'acrylate de méthyle, acrylate d'éthyle, acrylate de n- et isopropyle, acrylate de cyclohexyle, acrylate de triméthylcyclohexyle, acrylate de phényle, acrylate de benzyle et les méthacrylates correspondants ; acrylate et méthacrylate de furfuryle ; acrylate et méthacrylate de méthoxy-éthyl-, d'éthoxy-éthyl-, et d'éthoxy-éthoxy-éthyle ; acrylate et méthacrylate de 2-hydroxyéthyle ; acrylate, méthacrylate et méthylacrylamide de 3-hydroxypropyle ; méthacrylate de glycidyle ; N,N-diméthylacrylamide ; N-isopropyl-acrylamide ; N-vinylacétamide ; N-vinyl-pyrrolidone ; méthacrylate et méthylacrylamide de diméthylamino-éthyle ; acide acrylique et méthacrylique, acide vinylsulfonique, styrène, acide 4-styrène-sulfonique et acide 2-méthacrylamido-2-méthyl-propane-sulfonique et leurs sels, et de mélanges de ceux-ci.

33. Procédé selon la revendication 32, dans lequel le monomère est l'acrylate de méthoxy-éthyle et le méthacrylate de méthoxy-éthyle, l'acrylate d'éthoxy-éthyle et le méthacrylate d'éthoxy-éthyle ; le méthacrylate de méthyle ; l'acrylate de méthyle, le méthacrylate de 2-hydroxyéthyle ; la N-vinylpyrrolidone ; le N,N-diméthylacrylamide et le styrène et l'acrylate d'éthoxy-éthoxy-éthyle ou des mélanges de ceux-ci.
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34. Procédé selon la revendication 1, dans lequel le composant (C) est compris entre 5 et 60 % en poids dudit copolymère.
- 10 35. Procédé selon la revendication 34, dans lequel le composant (C) est compris entre 10 et 50 % en poids dudit copolymère.
36. Procédé selon la revendication 1, pour la fabrication d'une lentille de contact.
- 15 37. Procédé selon la revendication 1, dans lequel le polyéther PE est un polyéther fluoré de PM 600 à 5000 de structure HO-CH₂CF₂(C₂F₄O)_x(CF₂O)_yCF₂CH₂-OH, dans lequel x et y sont indépendamment l'un de l'autre des nombres entiers de 6 à 50.
38. Procédé selon la revendication 4, dans lequel la quantité de composant (C) est égale à zéro.
- 20 39. Procédé selon la revendication 4, dans lequel le composant (A) est compris entre 15 et 30 % en poids dudit copolymère.
40. Procédé selon la revendication 5, dans lequel le composant (A) est compris entre 30 et 60 % en poids dudit copolymère.
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41. Procédé selon la revendication 38, pour la fabrication d'une lentille de contact.
42. Utilisation d'un copolymère selon la revendication 1 pour la fabrication de lentilles de contact.
- 30 43. Lentille de contact constituée d'un copolymère comme défini dans la revendication 1.
44. Lentille de contact constituée essentiellement d'un copolymère comme défini dans la revendication 1.

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